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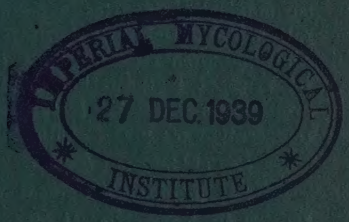
## (DOKLADY)

## DE L'ACADÉMIE DES SCIENCES DE L'URSS

NOUVELLE SÉRIE

1939

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1939. Volume XXIV, № 6

*MATHEMATICS*

# ON THE EIGENWERTE IN NORMED STRUCTURES

By G. M. SHAPIRO

*(Communicated by A. N. Kolmogoroff, Member of the Academy, 17. VI. 1939)*

The aim of the present note is to consider certain questions of the theory of Eigenwerte from the point of view of algebraical structures *. If we take the Eigenwerte of a symmetrical matrix, then the coincidence of two Eigenwerte is followed by the appearance of a set of Eigenvektors of proper dimensionality. A similar fact occurs in the general theory of Eigenwerte with the only difference that there the rôle of the dimensionality is played by another numerical invariant, namely the category ([2]). In both of these cases the domain of objects to which the theory is applied represents an algebraical structure, whose elements are linear subspaces, closed sets or closed families of curves. Hereby to every element of the structure corresponds a certain number (the maximum of a quadratic form on the given linear subspace, the maximum of a certain function on the given closed set or the maximum of the length of the curve in the given family), which may be considered as the norm of the element. The norm satisfies the monotony condition, i. e., it increases with the element. The Eigenwerte are now defined as the lower bounds of the norms of elements satisfying a certain condition imposed on the dimensionality or the category.

This definition of the Eigenwerte retains its sense for any normed structure, for which a numerical characteristic is defined in such a way that it is a generalisation of the dimensionality or the category; this numerical characteristic we shall call the rank of the element of the structure **.

In the present note we show that those consequences which appear in different structures in the case of coincidence of two Eigenwerte, are rooted in one general property of normed structures.

We consider a structure in which there exists the «first» element 0 and for each pair $a$, $b$ with $a \sqsubset b$ there exists at least one supplementary element $x$, for which

$$a + x = b, \quad ax = 0.$$

Suppose that to each element $a$ of the structure two real numbers are referred: its rank $\rho(a)$ and its norm $\nu(a)$.

---

* For the definition and the fundamental properties of structures cf. e. g. ([1]) or ([1a]).

** The conception of the rank in a somewhat narrower sense is to be found in ([3]). Cf. also ([4], [5], [6]).

With respect to the rank $\rho$ we assume that

$$\rho(a+b) \leqslant \rho(a) + \rho(b).$$

With respect to the norm $\nu$ we assume that

$$\text{for } a \supset b, \quad \nu(a) \geqslant \nu(b).$$

We introduce now the conception of the sum of an infinite set of elements of the structure. Under the sum of an infinite set of elements we shall understand the least element (if it exists) containing all given elements *.

Consider now a set of elements different from zero, which we shall call singular (or Eigen-) elements; about these elements we shall assume that any set of singular elements contained in some definite element of the structure has a sum.

Consider the set of all elements of the structure having a rank $\geqslant \rho$. Denote the lower bound of the norms of the elements of this set by $c_\rho$. The number $c_\rho$ we shall call the Eigenwert of the structure corresponding to the index $\rho$.

The element of the rank $\geqslant \rho$ having the norm $c_\rho$ is called the minimal element (of the order $\rho$). Suppose that the following «axiom of existence» holds:

For every minimal element $a$ there exists at least one singular element $g$ such that $g$ is contained in $a$ (i. e, $g \subset a$).

Now we can establish the following

Theorem. *If we have*

$$c_\rho = c_{\rho+\sigma}$$

*and $a_{\rho+\sigma}$ is the minimal element of the order $\rho+\sigma$, then the sum of all singular elements contained in $a_{\rho+\sigma}$ has a rank $> \sigma$.*

Proof. Let $s$ be the sum of all singular elements entering into $a_{\rho+\sigma}$. Then $s \subset a_{\rho+\sigma}$ and, consequently, there exists an element $t$ such that $st = 0$ and

$$a_{\rho+\sigma} = s + t.$$

Suppose now that $\rho(s) \leqslant \sigma$. We have

$$\rho(s+t) \leqslant \rho(s) + \rho(t);$$

consequently, $\rho(t) \geqslant \rho$. On the other hand

$$\nu(t) \leqslant \nu(a_{\rho+\sigma}),$$
$$\nu(a_{\rho+\sigma}) = c_{\rho+\sigma} = c_\rho.$$

From these relations it follows that

$$\nu(t) = c_\rho,$$

i. e., that $t$ is a minimal element. But then $t$ contains a singular element, i. e., $st \neq 0$, which is impossible. Hence, the rank of the element $s$ must be $> \sigma$.

In particular, if the rank of any element is an integer (which in many applications is often the case), we obtain $\rho(s) \geqslant \sigma + 1$.

Received
25. VI. 1939.

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* Cf. (1), p. 44.

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*PHYSICS*

# SCATTERING OF FAST ELECTRONS THROUGH LARGE ANGLES

By A. I. ALICHANOV, Corresponding Member of the Academy, A. I. ALICHANIAN and M. S. KOZODAEW

The object of the present research was study of the single scattering, through an angle of 90°, of electrons with energies within 600 to 2000 ekV. The scattering of electrons with energies of the above order of magnitude has been investigated more than once by means of Wilson's cloud expansion chamber, but the results arrived at by different investigators are very contradictory. Some(1) believe that, in the case of lighter elements, the chance of the electron being scattered through a large angle is far greater (tens of times) than that predicted on Mott's formula deduced from quantum-mechanical considerations; others (2) are of the opinion that Mott's formula holds well for lighter elements, while in the case of heavy elements the chance of scattering is considerably less than according to the formula (7 times, for mercury); and still others (3) report a very good agreement of their experiments with Mott's formula.

Contrary to the above-cited investigations, in our experiments the scattering proceeded not in the gaseous phase, but in thin foils, the scattered electrons being registered by the coincidence of the simultaneous discharges in two Geiger-Müller counters. A homogeneous beam of electrons selected by Danysz's magnetic spectrograph impinged on a thin foil of the substance under investigation placed at an angle of 45° to the beam. The two counters were placed at an angle of 90° with respect to the beam. Fig. 1 shows schematically the part of the arrangement containing the scatterer and the counters.

All the scattering foils to be examined were attached to a frame which in its turn was fixed to a ground joint so that, without disturbing the vacuum, one or another of the foils could be brought into the path of the electron beam, or they could all be removed, and the number of electrons scattered by the walls could be measured.

To our great surprise, in order to be able to observe the single scattering of electrons with energies near 1000 ekV, it was imperative to use very thin scattering foils, the thickness of which, in the case of aluminium, had not to exceed 2.7 mg/cm$^2$. The scattering was considered single when the number of scattering electrons proved proportional to the thickness of the scatteree. For energies of 1000 ekV this proportionality could be observed only with foils thinner than 5.4 mg/cm$^2$.

Table 1 gives the ratio of the number of electrons scattered in a 5.4 mg/cm$^2$ thick foil to that in a thickness of 2.7 mg/cm$^2$ for different energies of the electrons.

For greater thicknesses of the foils (27 and 12 mg/cm², for instance) the divergence from proportionality becomes very pronounced. For electrons with energies of 1075 ekV, the ratio $\frac{N_2}{N_1}$ is then 5 instead of 2.2, as might be expected.

However, according to Wentzel's criterion for single scattering, foils of this order of thickness should prove quite suitable for the investigation of single scattering. M. Artzimovich of our Institute has made for us some calculations which show in a convincing way that divergences from the proportionality rule will occur exactly in those thicknesses for which they have been observed in our experiments.

Table 1

| Energy in ekV | $N_2/N_1$ |
|---|---|
| 855 | 2.8—3 |
| 1075 | 2.3—2.4 |
| 1150 | 2 —2.16 |

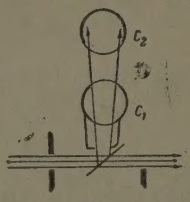

Fig. 1.

These calculations will shortly be published, so that we shall not dwell on the subject, giving only the final results.

According to Artzimovich, the divergence from proportionality is due to the fact that to those electrons which have undergone single scattering, are admixed to a large extent such as have been first scattered through a large angle, say 70°, and then deflected owing to multiple scattering through a definite angle, say 20°. The number of electrons scattered by a aluminium foil of the thickness $x$ is, in arbitrary units:

$$N = x + \frac{1.510^{-2}x^2}{E^2}$$

where $E$, the energy of the electrons, is expressed in megavolts, and $x$ in microns*. For $E = 1$ MeV, $x = 10$, $N_1 = 10 + 1.5 = 11.5$. For $x = 20$, $N_2 = 20 + 6 = 26$, i. e. $\frac{N_2}{N_1} = 2.26$.

The following substances have been investigated:

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Celluloid | 1.55 | mg/cm² | in | the | energy | interval | 585— 855 | ekV |
| » | 3 | » | » | » | » | » | 855—1180 | » |
| » | 6 | » | » | » | » | » | 1050—1600 | » |
| Aluminium | 1.55 | » | » | » | » | » | 585—1050 | » |
| » | 2.7 | » | » | » | » | » | 815—1180 | » |
| » | 5.4 | » | « | » | » | » | 1080—1600 | » |
| Copper | 1.33 | » | » | » | » | » | 855—1375 | » |
| Gold | 0.51 | » | » | » | » | » | 855—1375 | » |
| » | 1.15 | » | » | » | | » | 1180—2060 | » |

Curve of Fig. 2 shows the theoretical relation according Mott's formula between the amount of scattering and the energy of the electrons.

The points shown in Fig. 2 together with Mott's theoretical curve are the experimental data for celluloid, Al, Cu and Au. The relation between the amount of scattering and the atomic number of the given substance is seen from Table 2, the accuracy of the experimental data being 15%.

The theoretical values have been deduced from Mott's formula taking into account the term proportional to $Z^3$, i. e. from

$$\sigma = kZ^2\left(\operatorname{csc}^4\frac{\Theta}{2} - \beta^2\operatorname{csc}^2\frac{\Theta}{2} + \beta\frac{\pi Z}{137}\frac{\cos^2\frac{\Theta}{2}}{\sin^3\frac{\Theta}{2}}\right). \qquad (1)$$

* The above formula holds only for low values of the second term, it is for low values of $x$, or high values of $E$.

For gold, for the scattering through an angle of 90°, Mott gives the following formula

$$\sigma = kZ^2 \left( \operatorname{csc}^4 \frac{\theta}{2} \right) R, \qquad (2)$$

where $R=3.2$ for energies of ca 1000 ekV. The theoretical value for gold is seen to be 2.3 times that obtained from experiment, the discrepancy exceeding the limits of experimental error. The figure in brackets (Table 2) has been obtained with the aid of the approximate formula (1).

If we estimate the chance of scattering from the geometry of the apparatus used, the following results are obtained.

The probability that by an aluminium foil of the thickness of 2.7 mg/cm² the electrons will be scattered through angles between 82 and

Table 2

| Substance | Z | $\sigma_{exp}$ | $\sigma_{theor}$ |
|---|---|---|---|
| Celluloid . | 7.1 | 0.31 | 0.29 |
| Aluminium | 13 | 0 | 1 |
| Copper . . | 29 | 5.6 | 6 |
| Gold . . . | 79 | 78 | 178 (67) |

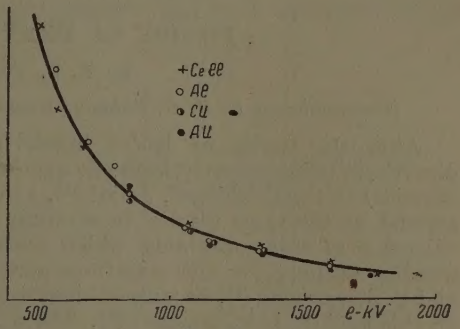

Fig. 2.

97° at $\beta=0.95$ is equal to $1.54\times10^{-4}$; the corresponding value calculated from Mott's formula is $1.85\times10^{-4}$. This estimate is not very accurate and only shows that there is no very pronounced discrepancy between this and the theoretical result.

To conclude, it can be said that, within the limits of experimental error, the large angle scattering of electrons with energies of the order of 1000 ekV is in good agreement with quantum-mechanical considerations.

Gold is an exception, here the scattering has been found to be 2.3 times less (in comparison with aluminium) than it follows from expression (2) deduced by Mott especially for angle of 90°.

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*PHYSICS*

# FISSION OF URANIUM NUCLEI

By N. F. VOLKOV

*(Communicated by V. G. Chlopin, Member of the Academy, 26. VI. 1939)*

After the fission of heavy nuclei of uranium and thorium has been discovered independently from one another by Hahn and Strassmann (1) by a chemical method, while F. Joliot (2), as well as L. Meitner and O. Frisch (3) arrived at the same results in a purely physical way, the problem of the existence of trans-uraniums which seemed to be positively solved by a number of previous investigations, particularly by O. Hahn, L. Meitner and F. Strassmann (4), became dubious again. At the present time the opinion on this subject is at variance (5). The majority of investigators are inclined to believe that out of all the trans-uraniums previously described there must unquestionably exist but one which is due to the resonance-capture of a neutron by the nucleus of uranium 238.

$$^{238}_{92}U + {}^{1}_{0}n \rightarrow {}^{239}_{92}U; \qquad {}^{239}_{92}U \rightarrow \text{eka-Re} + e.$$

Eka-rhenium which is produced in the course of this reaction may be stable, or else, it may go on disintegrating, both with the emission of β-particles (which is less probable) and α-particles.

We thought it possible to approach the problem of the existence of trans-uraniums proceeding from the following considerations. The theoretical conceptions of Bohr (6) which explain the process of the fission of uranium and thorium nuclei, seemed to us not to exclude the probability of nuclei of elements still heavier than uranium, i. e. transuraniums, being similarly subjected to fission. Therefore, if one would succeed in establishing experimentally that the process of nuclear fission proceeds not only at the very moment of the bombardment of uranium with neutrons, but somewhat after the bombardment has ceased, this could be taken as a proof of the existence of trans-uraniums.

To check this assumption the following experiments have been arranged by us.

1. 62 g sodium uranate were during 24 hours subjected to bombardment from a source of neutrons obtained on the cyclotron of the Radium Institute of the Academy of Sciences according to the reaction ${}^{2}_{1}D + {}^{2}_{1}D \rightarrow {}^{3}_{2}H + {}^{1}_{0}n$. The intensity of the flow of neutrons equaled approximately 20 Curie Rn + Be. After the end of bombardment, the sodium uranate was scattered over an area of 3500 cm², and two layers of tissue-paper were placed at a distance of 7—10 mm from the surface of uranium. The paper was kept over the uranium for 5 hours, after which it was incinerated and the ash obtained was subjected to measurements by means of a Geiger-Müller counter. The

ash showed an appreciable activity. Fig. 1 represents the curve of the decay of its activity, of which we succeeded to take a photograph. After a 5-hour exposure, one layer of the tissue paper was taken for examination and replaced by a fresh one. Thus, the recoil atoms were collected 5 times after 5-hour intervals. In each case the ash obtained from the burned tissue paper showed an activity which was gradually decreasing. The half-life equaled 6.5 hours. Fig. 2 shows the logarithmical curve of the activity drop. The experiment was repeated several times, the phenomenon being always reproduced.

2. To bombardment was subjected green uranium oxide, 1 g of which was spread in the form of a thin layer over a surface of 700 $cm^2$ surrounded with paraffin. The bombardment lasted 24 hours, the intensity of the neutron flow being the same as in the previous experiment. After the bombardment was ended, glass plates were placed 3 mm over the surface of ura-

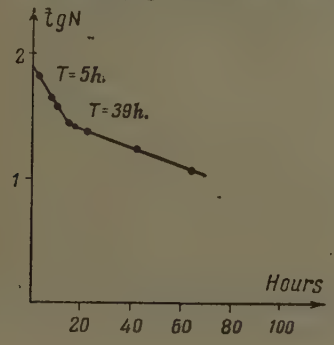

Fig. 1.

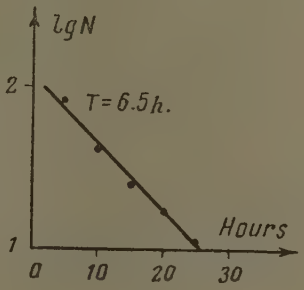

Fig. 2.

nium. 4 hours later they were removed and their surface which had faced the uranium was wiped with filter paper soaked in 7% hydrochloric acid. The paper was then dried and subjected to measurement. It always proved active, showing the same 6.5-hour half-life as in the preceding experiment. By the value of the activity obtained one could conclude that it does not depend on the absolute quantity of uranium, but on the surface of the source.

A control experiment on uranium withheld from neutron bombardment for several days gave no activity whatsoever, either on paper or on glass.

To find out the causes responsible for the activity of paper and glass observed in the two first cases, the next additional experiment was arranged.

3. On glass plates were collected products of fission of uranium nucleus under the action of neutrons according to the method of radioactive recoil, as described in the article by V. G. Chlopin, M. A. Passvick-Chlopina and N. F. Volkov (7). The exposure of uranium to neutron bombardment lasted 24 hours, the intensity being about 20 Curie Rn + Be. After the end of bombardment, the glasses were carefully removed and covered with two layers of tissue paper which was kept in place for 4 hours. After the end of exposure, the paper was removed, and the sheets which had been in direct contact with the glass and those which constituted the second layer were burned separately. The ashes were collected apart and measured for activity. Both samples proved active, their activity decreasing in such a way that it was possible to differentiate on the curve two products with half-lifes of 4 and 19 hours, respectively.

The results obtained by us may be interpreted proceeding from the following assumptions:

a) Some of the uranium nuclei fail to divide at once after the capture of neutrons, doing so not until a certain lapse of time. The same characteristic is proper to some heavy products of the fission of uranium nuclei.

b) There takes place no slow process of subsequent fission of the uranium nuclei and of their heavy products of decay, but there is simply formed among the products of the uranium nuclei fission a gaseous radio-element with a rather long half-life, located somewhere in the middle of the chain of decay.

To find out which of these two interpretations is correct, a separate series of special experiments has been arranged at this Institute. These will involve, on the one hand, examination of the tracks of the products of subsequent fission of the uranium nuclei and of its heavy products by the method of differential counters, by that of Wilson's cloud chamber of reduced pressure and by the method of thick-layered photoplates; on the other hand, these experiments will aim at the discovery of the hypothetical gaseous product of decay and at the determination of its chemical nature.

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*PHYSICS*

# ON THE DISTRIBUTION OF ELECTRONS OVER THE SECTION OF A GAS DISCHARGE

By V. FABRIKANT

*(Communicated by S. I. Wawilow, Member of the Academy, 28. VI. 1939)*

Like all diffusion theories, Schottky's (1) theory of the positive column of a gas discharge is only valid so long as the lengths of the free paths of the elementary particles are sufficient small.

However, under the given conditions the assumption of the direct nature of the process of ionization, which forms the basis of Schottky's theory, is usually not observed. Experimental data afford evidence that under these conditions a considerable part is played by cumulative ionization, i. e., the ionization of atoms already excited (2).

Assuming that at every point in the discharge the concentration of excited atoms is proportional to the concentration of electrons, Schottky showed that to take the cumulative ionization into account is equivalent to the solution of a non-linear differential equation with constant coefficients.

Schottky did not give the solution of this differential equation. In view of the circumstance, indicated above, that Schottky's theory must generally be applied when the conditions are such that intense cumulative ionization is present, we considered that it would be of interest to elucidate the manner in which the presence of cumulative ionization influences the validity of certain conclusions drawn from this theory.

1) For the sake of simplicity we will consider the problem under the same boundary conditions as taken by Schottky, i. e., we will assume that the concentration of electrons at the walls is zero. The question of the boundary conditions is considered more strictly in Granovsky's (3) work in which it is shown that the treatment of this problem given by Funk and Seelinger (4) is erroneous. We shall at once confine ourselves to the limiting case in which all the ionization takes place in a cumulative manner.

Our assumption concerning the concentration of the excited atoms differs from that of Schottky and is that this concentration is distributed over the section of the discharge according to a Bessel function of zero order and is zero at the walls (11). Then, if there is no volume recombination, we obtain for the concentration of the electrons:

$$\frac{1}{x}\frac{d}{dx}\left(x\frac{dn_e}{dx}\right)+b_1 J_0(\mu_1 x)\, n_e = 0 \qquad (1)$$

where $n_e$ is the electron concentration, $x=\frac{r}{a}$, $a$ is the radius of the discharge tube, $\mu_1$—the first root of the Bessel function, $b_1=\frac{\alpha_i' \cdot a^2}{D}$, where $\alpha_i'$ is the number of cumulative ionizations per electron on the axis of the discharge, $D$—the coefficient of ambipolar diffusion. Equ. (1) is a uniform linear differential equation with variable coefficients. This equation may be solved either

by development into a series of powers, or graphically. First of all we determine the proper value of the parameter $b_1$ from the boundary conditions.

Both the analytical calculation carried out at our request by K. A. Semendjaev and the graphical integration which we effected by Frank's [5] method of functional scales give the value of $b_1$ as close to 7.2. Instead of the expression obtained by Schottky:

$$a\sqrt{\frac{\alpha_i}{D}} \approx 2.4 \qquad (2)$$

where $\alpha_i$ is the number of direct ionizations per electron we obtain:

$$a\sqrt{\frac{\alpha'_i}{D}} \approx 2.7. \qquad (3)$$

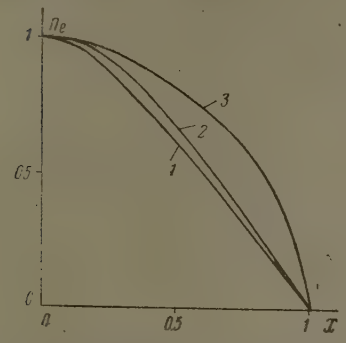


Fig. 1. *1*—electron distribution with cumulative ionization; *2*—electron distribution with direct ionization; *3*—electron distribution with recombination during triple collisions.

Expression (3) is essentially more complicated than (2) since $\alpha'_i$ is proportional to the concentration of excited atoms on the axis of the discharge.

2) Curve *1* (Fig. 1) represents the solution of equation (1), curve *2* that of a zero order Bessel function with zero at the wall, corresponding to direct ionization. It will be seen that the solution of equation (1) in practice approaches very closely to a zero order Bessel function.

It should be borne in mind that we have considered the limiting case in which all the ionization is cumulative and when the divergence should be greatest. We thus come to the very important conclusion that the nature of the ionization has very little influence on the distribution of electrons over the section of the discharge. If the ionization is cumulative we may, with sufficient accuracy, employ the same expression for the distribution of electrons over the section of the discharge as in the case of direct ionization:

$$n_e(r) = n_e(0)\, J_0\left(\mu_1 \frac{r}{a}\right). \qquad (4)$$

There will be considerable difference only in the magnitude of $n_e(0)$ and in the number of pairs of ions formed per unit volume per unit time.

The distribution of the number of newly formed ions will be close to $J_0^2\left(\mu_1 \frac{r}{a}\right)$ [3].

3) If we confine ourselves to the limiting case, it is easy to examine how volume recombination ought to influence the distribution of electrons over the section of the discharge.

Recombination may be of two types, either on double collision (ion and electron) or triple (ion and two electrons). Since the number of acts of recombination is proportional to the square or the cube of the concentration, volume recombination will be more intense on the axis of the discharge. The distribution curve of the electrons should therefore be rendered more convex by the presence of volume recombination. If the ionization takes place in a cumulative manner only and the destruction of charges takes place only owing to recombination on double collision, and diffusion to the walls may be neglected, we may write in place of (1):

$$-n_e^2 + b_2 J_0\left(\mu_1 \frac{r}{a}\right) n_e = 0. \qquad (5)$$

Equation (4) is now an accurate expression for $n_e(r)$. The constant $b_2$ is equal to the concentration on the axis of the discharge and, naturally, depends on the probability of recombination. For volume recombination due to triple collisions, for the same limiting case, we obtain:

$$-n_e^3 + b_3 J_0\left(\mu_1 \frac{r}{a}\right) n_e = 0 \qquad (6)$$

or

$$n_e(r) = n_e(0) \sqrt{J_0\left(\mu_1 \frac{r}{a}\right)} . \qquad (7)$$

Curve *3* (Fig. 1) represents the electron distribution in this limiting case. We here observe considerable divergence from curve *2*. It should be borne in mind that recombination within the volume commences to play its part under discharge conditions close to the equilibrium temperature, when a number of the assumptions made in the theory become incorrect.

4) In works on discharge in gases it is frequently omitted from view that, according to the principle of micro-equilibrium temperature, equilibrium for ionization processes should be attained when the number of acts of ionization due to collisions between electrons is equal to the number of acts of volume recombination on triple collision ([6]). Only under these conditions is it permissible to apply Saha's formula for the ion concentration. This is to be explained by the circumstance that the principal process causing ionization is collision between electrons and not a volume photo-effect.

Triple collisions leading to the formation of excited ions have not been studied at all. They are processes of reversible cumulative ionization and may play a considerable part in the discharge. Therefore it would be of interest to examine the results of investigations on discharge in caesium vapour ([7]).

5) In a recent work Riewe and Rompe ([8]) indicate that if ionization is taken into account it may lead to a marked reduction in the limiting concentrations of excited atoms in a mercury-vapour discharge found by us earlier ([9]). Riewe and Rompe did not take into account the circumstance that in a discharge equilibrium does not set in simultaneously on different levels.

Our calculations related to the very lowest excitation level ($6^3P_{0,1,2}$), on which equilibrium sets in first of all. The application of Saha's formula, used by Riewe and Rompe, is only permissible under conditions when there is also equilibrium of ionization processes (ionization and triple collision), which only sets in considerably later. The choice of limiting concentrations was therefore a rational one for our conditions, as was confirmed by further experiments ([10]) and calculations ([11]). Use of the limiting concentrations proposed by Riewe and Rompe would render it impossible to draw any conclusions as to whether the excitation conditions for the given level are close to equilibrium or not.

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*PHYSIQUE DU GLOBE*

# ÉCLAIREMENT DE LA SURFACE TERRESTRE PAR LES ONDES LUMINEUSES COURTES ET LONGUES DE LA VOÛTE CÉLESTE

Par N. N. KALITINE

*(Présenté par A. A. Grigorieff, de l'Académie, le 26. VI. 1939)*

Les observations de Prist(1) de la température de couleur équivalente de la voûte céleste ont montré que pour le ciel sans nuages cette température varie de 25000 à 8000° suivant l'état de l'atmosphère. Pour la voûte céleste entièrement couverte de nuages cette température est de l'ordre de 6000°. Par conséquent,la température de couleur équivalente peut servir d'un parfait indiquateur de l'état de l'atmosphère (le ciel sans nuages et le ciel nuageux).

Pour la détermination de la température de couleur équivalente il faut effectuer des mesures spectrophotométriques(2), ou bien, ce qui est encore mieux—spectrobalographiques. Mais ces mesures peuvent être remplacées, avec une précision suffisante pour les buts pratiques de la géophysique, par les mesures du rapport des éclairements dans les différentes parties du spectre au moyen d'un élément photoélectrique muni d'un filtre.

Un élément photoélectrique de sélénium muni d'un filtre coupant les parties extrêmes du spectre et lié au galvanomètre de la sensibilité de l'ordre de $10^{-6}$ ampères est le plus approprié à cet emploi.

Dans la première moitié de l'année 1939 à Sloutzk (près de Léningrad) ont été effectuées les mesures du rapport entre l'éclairement de la surface horizontale en rayons bleux ($b$) et l'éclairement de la même surface en rayons rouges ($r$), c.-à.-d. la valeur de $b/r$. L'élément photoélectrique et les filtres, utilisés à ce but, ont été les mêmes dont je me suis déjà servi pour l'étude de l'albedo spectral de la couverture de neige(3). La sensibilité spectrale d'un photoélément de sélénium pour un filtre bleu était bornée par les longueurs d'ondes 3600—5100 Å avec le maximum aux environs de 4500 Å, et pour un filtre rouge de 6000 à 7300 Å avec un maximum aux environs de 6100 Å. Le photoélément était monté de façon à permettre les mesures des éclairements de la région zénithale de la voûte céleste dans un angle visuel de 60°, c.-à.-d. dans un cercle ayant le point de zénithe pour centre et un rayon de 30°. Dans un tableau nous donnons les rapports des grandeurs lues à l'échelle du galvanomètre pour l'écran bleu et pour l'écran rouge ($b/r$).

Pour exclure l'influence de la hauteur du soleil sur la structure spectrale de l'éclairement, les mesures ont été faites pour la hauteur de 30°.

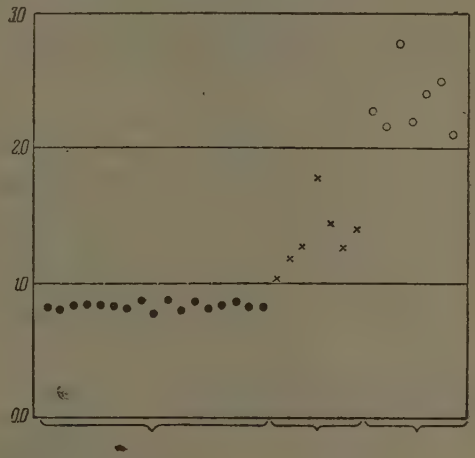
Pour savoir, quel était l'état de nuages dans le champ de l'appareil au moment de l'observation, un instrument spécial indiquait, d'après l'échelle admise généralement, l'état de nuages dans ce champ visuel; 10 désignant le champ entièrement couvert de nuages et 0—absence totale de nuages.

Les observations effectuées par moi, il est vrai, dans une quantité non suffisante, montrent que pour la voûte céleste entièrement couverte de

nuages des formes basses on obtient le rapport $b/r = 0.83$ (17 observations) et pour le ciel sans nuages $b/r = 2.38$ (7 observations). Pour la voûte céleste non entièrement couverte de nuages on obtient les valeurs intermédiaires, le rapport étant plus grand pour le ciel plus dégagé.

Il est intéressant à noter que le rapport $b/r$, obtenu par moi pour le ciel sans nuages, correspond exactement au rapport des éclairements avec les longueurs d'ondes du maximum de transparence des filtres suivant la courbe moyenne des éclairements du ciel sans nuages, citée dans l'article (2) et obtenue par la méthode de spectrophotométrie. Les petits ronds noirs sur la figure désignent les valeurs $b/r$ pour le ciel couvert, les croix—les mêmes valeurs correspondant au ciel non entièrement couvert et les petits ronds blancs—au ciel complètement dégagé. On voit que le ciel couvert et le ciel dégagé donnent deux groupes nettement distincts de points.

| Temps de l'observation | $b/r$ | État de nuages dans le champ de l'appareil |
|---|---|---|
| 1939 | État de nuages 10 | |
| Mars 21 | 0.81 | 10 St |
| » 24 | 0.84 | 10 St |
| » 25 | 0.83 | 10 Sc |
| » 27 | 0.78 | 10 (brume) |
| Avril 2 | 0.86 | 10 St |
| » 14 | 0.82 | 10 St |
| | État de nuages variable | |
| Mars 27 | 1.02 | 8 Ac |
| » 31 | 1.28 | 7 Cs |
| Avril 4 | 1.36 | 3 Ci |
| » 11 | 1.44 | 7 Ac° |
| | Pas de nuages | |
| Mars 29 | 2.27 | 0 — |
| Avril 3 | 2.16 | 0 — |
| » 8 | 2.78 | 0 — |
| Juin 6 | 2.40 | 0 — |
| » 8 | 2.50 | 0 — |




Il faut noter, que pour le ciel entièrement couvert de nuages du type Ci nous allons obtenir les valeurs de $b/r$ suffisamment voisines de celles du ciel dégagé, ce qui est encore très important. Les variations observées des valeurs relatives au ciel dégagé nous indiqueront les changements des propriétés diffusantes de l'atmosphère, ce qui a une grande valeur aussi bien théorique que pratique (la caractéristique des masses d'air).

Les observations systématiques des rapports des éclairements dans les différentes parties du spectre peuvent être également très importantes pour la photographie, surtout pour la photographie aérienne. Les observations peuvent être simplifiées en mesurant la valeur du rapport des éclairements directement par un lagomètre ou en les enregistrant par son intermédiaire.

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*BIOPHYSICS*

# RECORDING OF THE DOLPHIN'S BODY MOVEMENT IN THE SEA

By I. I. STASS

*(Communicated by P. P. Lazarev, Member of the Academy, 25. VI. 1939)*

The mechanism of the movement of the dolphin has long since attracted the attention of investigators: to develop the tremendous velocity of about 10 m/sec. the dolphin must possess not only a good flown around shape of the body (1), but a perfect propeller too.

The difficulty of immediate visual observations of the dolphin's movement in the sea, which is due to the considerable frequency of oscillations and the optic distortions in the water, has led to various and contradictory interpretations of its mechanism. On one hand, Houssay (2) and most of the hydrobiologists with him think till the present time that the dolphin moves by means of vertical oscillations of the tail fin. On the other hand, Shoulejkin(3) has come to the conclusion that the whole body of the dolphin presents a propeller, along which runs a wave polarized to a circle or an ellipsis: each transversal section of the body performs oscillations both in vertical and horizontal plane. Shoulejkin has discovered the presence of such movements of the dolphin by cinemographing a dolphin, the front part of which was fixed in a frame; the larger part turned to the cinema-apparatus could move freely in the air. Shoulejkin came to the same conclusion by an indirect way too, e. g. by considering the asymmetrical head of the dolphin in its rapid movement in the water as a certain compensator preventing the constant rotation of the dolphin's body around its longitudinal axis.

Howewer, as it has been mentioned above, the greater part of hydrobiologists did not agree with the conclusions of the physicist. The old supposition was supported even by Narkhov (4) who has made a detailed investigation on the anatomy of dolphin muscles and discovered that muscle ilio-costalis with its one-sided contraction lifts the tail and simultaneously abducts it, while muscle ischio-caudalis bends it downward abducting it at the same time; in short, these muscles obviously perform the body's simultaneous movement not only in the vertical, but also in the horizontal direction. In spite of this, Narkhov continued to believe that the dolphin's movement is performed by means of the tail-fin rapidly vibrating in the vertical direction (by the way, we can calculate that to work according to this scheme the dolphin should develop such a tremendous frequency of vibration that, when in motion, it would hum like a bumble-bee).

Defending the hypothesis of vertical oscillations, some investigators pointed ouf that Shoulejkin's experiments were made in the air medium and that the dolphin's body in these experiments could have moved quite diffe-

rently from what it would be in the water. Though such a denial of habitual reflex movements of the dolphin is evidently of no value in itself, it is, however, of interest to disprove the obsolete opinions by means of immediate experiments in the sea: i. e. by means of direct recording of the vibrations of the tail of the dolphin, while moving in its natural medium—sea water.

The present article contains a description of such an immediate record made by means of a specially designed self-recording apparatus. The scheme

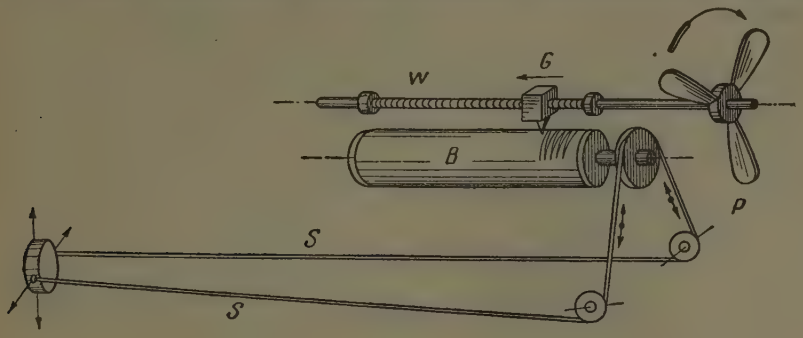


Fig. 1.

of the latter is shown in Fig. 1; its position on the dolphin's back can be seen in Fig. 2.

Drum $B$ could be made rotate by horizontal vibrations of the tail through alternative tension of the right and left string $S$. The tips of the string were

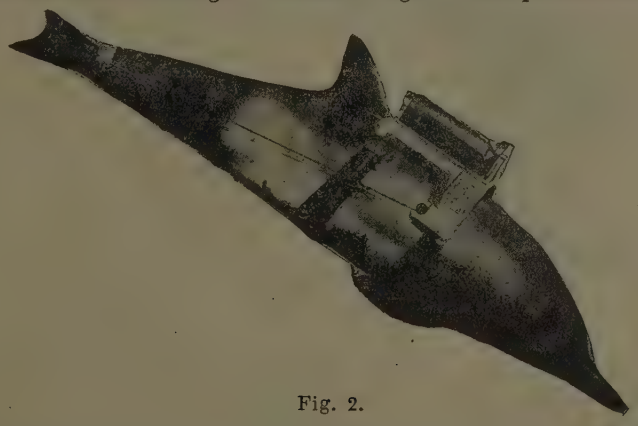

Fig. 2.

fixed to a bracelet put around the tail just before the fin. A rubber band was used for a reliable tension of the string. Above the drum was put nut $G$, through which was passed a long thin screw $W$ with a very fine thread, connected in front with the propeller $P$ having a considerable step. A sheet of thin paper covered with a layer of wax was put on the drum. The wax was scratched by a sharp needle placed under nut $G$. If the alternative tension of the right and left string $S$ did not make the drum turn to one and another side around its axis, the needle would have traced a straight line on the surface of the wax, since the movements of the dolphin in water would make the propeller with the screw revolve and move the nut paralell to the axis of the drum.

Control observations have shown that direct up-and-down movements of the dolphin's tail did not cause any revolutions of the drum around its axis. Consequently, had the dolphin worked with its propeller according to the old scheme suggested by the biologists, then after the swim in the water a straight line would have been traced on the drum. In fact the picture obtained proved to agree with the physical scheme.

The dolphin was let into water from board of the expedition ship «J. Shokalski» on a log-line 100 m long. After a swim of 100 m the animal was drawn on board and the waxed paper taken off. On this paper we found perfectly clearly recorded traces of the horizontal vibrations of the tail, reproduced from the original in Fig. 3. We were obliged to take Fig. 3 with an oblique position of the paper, in order to distinguish better the dark traces against the light background of the shining wax surface.

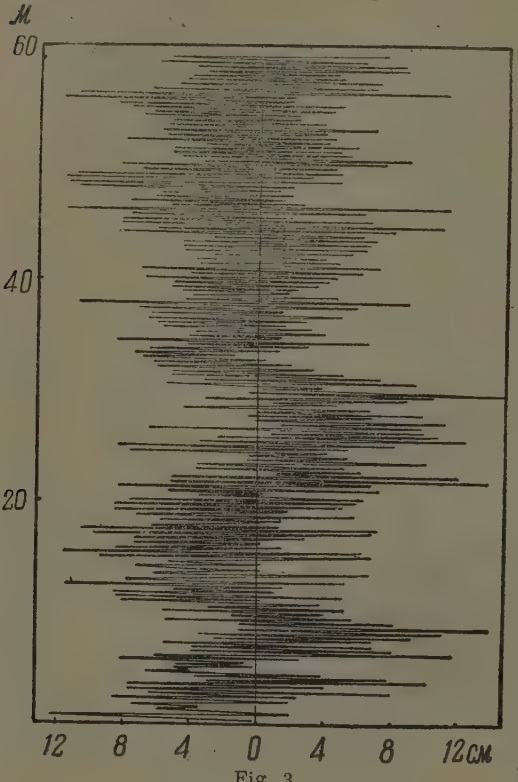

Fig. 3.

The photos show that the dolphin performed the vibrations of the tail in the horizontal direction, the deviations from the diameter plane attaining the mean value of 8 cm. The amplitude of purely vibrating movements reached about cm 6. Besides, the body of the dolphin bent somewhat in the horizontal direction when its way in the water swerved to the right or to the left from the predominant direction. The traces of such a movement are recorded by the readings as large slanting waves. The scale of the records for the vibrations was determined directly by means of abducting the tail to a certain distance from the diameter-plane of the body. The scale of the longitudinal distance swum was controlled by means of the dragging of the apparatus along a channel at the same rate which the dolphin had shown during the experiments. In its turn the latter value was determined with the aid of a stop-watch and proved to be 70 cm/sec. Under the movement with this velocity the nut took 86 sec. to pass from stop to stop along the screw, this period corresponding to the distance swum of 60 m.

For the dolphin of the experiment which had the length of 140 cm the normal velocity may be taken equal to 100 cm/sec. Consequently, the movement of the dolphin with the apparatus on its back was 30% below the usual. The frequency of vibrations (full) proved equal to 1.7 per second, which corresponds to the period of vibrations (full) of 0.6 sec. It stands to reason that the presence of the self-recorder on the dolphin's back,

as well as the bracelet, straps and other auxiliary details, largely reduced the flown-around shape of its body, and therefore the numerical value of the hydrodynamic characteristics had to diverge from the natural one. But it is also clear that this circumstance has no importance for the solution of the problem we have to solve: the immediate recording has shown the existence of horizontal vibrations of the dolphin's body, thus confirming Shoulejkin's hypothesis and disproving the scheme of the advocates of purely vertical vibrations. As the existence of the latter has never been and is not questioned by anybody, their recording was not included in the scope of the present work. In future, however, we shall try and record the vertical vibrations, too, in order to solve the question, whether the wave running along the dolphin's body is polarized to the circle or to the ellipsis.

Naturally enough, to carry out such a complex recording the design of the apparatus must be much more complicated than that presently applied.

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*PHYSICAL CHEMISTRY*

# ON THE «CHIEF» AND «AUXILIARY» VALENCY IN COMPLEX COMPOUNDS AND MOBILITY OF THE CO-ORDINATED PARTICLES

By A. POLESSITSKY

*(Communicated by V. G. Chlopin, Member of the Academy, 19. VI. 1939)*

Classical Werner's scheme of the formation of the complex compound:

$$AX_2 + BX_2 \rightarrow A\left[X - \begin{matrix} X \\ \vdots \\ B \\ \vdots \\ X \end{matrix} - X\right]$$

postulated two types of chemical bond between central atom and co-ordinated particles, realized by «chief» and «auxiliary» valency. This scheme was abandoned by Werner himself, since chemical properties of all co-ordinated particles were found to be identical and their distances from the central atom, as measured by X-rays diffraction, equal to one another. Recently, however, Grew stated non-equality of the outer particles. It was, therefore, of interest to test this problem by the method of «marked» atoms, with artificial radioelements as indicators.

Following reaction of formation and decomposition of a complex was studied:

$$HgI_2 + 2KI \rightarrow K_2HgI_4 \rightarrow Ag_2HgI_4 \rightarrow 2AgI + HgI_2.$$

One of the components ($HgI_2$ or KI) contained some radioactive iodine I*, obtained through irradiation of $C_2H_5I$ by slow neutrons and extraction by water containing some traces of KI. Practically the whole I* passed into water layer and activated KI.

To separate the end products AgI and $HgI_2$ from one another, the latter was extracted by KI solution and reprecipitated as $Ag_2HgI_4$ by $AgNO_3$; then both were measured on Geiger-Müller counter.

If the bonds between the central atom and co-ordinated particles are of different types, each of the metallic atoms will on decomposition leave the complex with the iodine atoms it was combined with before the formation of the complex, and all the radioactive atoms will remain in the same component in which they were before the reaction, while the second component will be non-radioactive. In the opposite case radioactive iodine atoms will be equally distributed between both components, though before the reaction they were combined with one of them. The results of the experiments were as follows (Table 1).

These results show the equivalency of the four iodine atoms.

The method of «marked» atoms make it possible to study the mobility of the co-ordinated atoms and their exchange with the surrounding medium.

Table 1

| | Radioactivity before the reaction | | Radioactivity after the reaction | |
|---|---|---|---|---|
| | KI | $HgI_2$ | KI (as AgI) | $HgI_2$ (as $Ag_2HgI_4$) |
| 1 | 100% | 0 | 44% | 56% |
| 2 | 0 | 100% | 43% | 57% |

For that purpose either KI* was added to a solution of $K_2HgI_4$ or, conversely, $K_2HgI_4$* was added to KI, and the mixture thus obtained was boiled. If there were an exchange, the radioactive iodine atoms would be distributed between both substances; in the opposite case they would remain in the same substance, in which they had been before mixing.

To separate the mixture KI was precipitated with strictly equivalent amount of $AgNO_3$, and $K_2HgI_4$ in filtrate with an excess of $AgNO_3$. The results of two experiments with equivalent quantities of $K_2HgI_4$ and KI boiled during 10 min. are given hereafter (Table 2).

Table 2

| | Radioactivity before reaction | | Radioactivity after separation | |
|---|---|---|---|---|
| | KI | $K_2HgI_4$ | KI (as AgI) | $K_2HgI_4$ (as $Ag_2HgI_4$) |
| 1 | 100% | 0 | 44% | 56% |
| 2 | 0 | 100% | 54% | 46% |

These data show that there is a rapid exchange between the iodine in the complex compound and the free iodine ions. A proportional distribution of the radioactive atoms between both compounds shows that all iodine atoms of the complex take part in the exchange. It is an additional evidence of the equivalency of all iodine atoms in the complex.

Experiments with varying quantity of compounds, varying duration of exchange and various methods of separating the compounds gave the same results.

An interesting point to note here is that when $HgI_2$ was separated from AgI by solution in the excess of KI, the residual AgI contained always less radioactive atoms than it was expected to contain (e. g., 43—44% instead of 50% in the first experiment). This could be explained by a partial exchange of iodine atoms between the solid AgI and the excessive KI added to dissolve $HgI_2$. As a matter of fact the experiment showed that a fresh precipitated well coagulated AgI, boiled during 30 min. with a solution containing an equivalent amount of KI, lost a half of its radioactivity, and this corresponds to a full exchange. The same result showed AgBr in KBr in solution.

An «altered» precipitate showed a much slower exchange, While the co-ordinated halogen ions show an easy exchange, halogens as central atoms in complexes exhibit different properties. No exchange of iodine atoms was stated between $IO_3^-$ and I' boiled during 3 hours (a longer boiling was impossible on account of the short life of the radioactive iodine), and no exchange of bromine between $BrO_3^-$ and Br boiled during 8 days.

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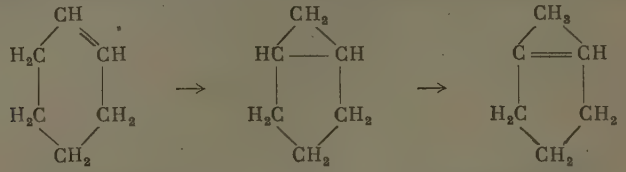
*CHEMISTRY*

## CONTACT ISOMERIZATION OF MENTHENE

By N. D. ZELINSKY, Member of the Academy, and J. A. ARBUSOV

We have shown recently (1) that cyclohexene when brought into contact with aluminium oxide at a temperature of 400 and 450° was being isomerized into methyl-cyclopentene. 1-Methyl-cycloxene-3 under the same conditions was isomerized into dimethyl-cyclopentene. In order to explain the mechanism of these transformations, the following scheme was proposed by us:



It was to be expected that in the case of more complex cyclohexene derivatives a similar transformation of the six-membered unsaturated cycle into a five-membered unsaturated one would take place.

It seemed interesting to spread this observation upon monocyclic terpene hydrocarbons, containing a six-membered unsaturated cycle, as well as upon bicyclic terpene hydrocarbons containing a tetramethylene cycle (pinane) and a trimethylene one (carane, thuyane).

In the first place we carried out experiments dealing with the contact transformation of menthene. *p*-Menthene-3 was prepared through the dehydration of *l*-menthol over silica gel at 325°. The hydrocarbon obtained had b. p. 166—168°/735 mm; $n_D^{20} = 1.4527$; $d_4^{20} = 0.8161$; $[\alpha]_D = +9.56$.

Menthene (55.7 g) was brought into contact with silica gel at a temperature of 375° at a rate of 6 g per hour. The inside diameter of the reaction tube was 15 mm; the length of the silica gel layer—60 cm. The condensate obtained (54.6 g) was fractionated over metallic sodium and separated into two parts: 1) 150—164°, 22.0 g; 2) 164—172°, 29.2 g. Fraction 164—172° was again brought into contact with silica gel. The condensate (28.5 g) was again distilled and the main part was collected (26 g) which passed over from 150 to 172°.

Fraction 150—164° after the first passage, and fraction 150—172° after the second were united and the product was subjected to fractional distillation over sodium. It was obtained: 1) 150—158°, 5.7 g, $n_D^{25} = 1.4414$; 2) 158—165°, 30.6 g, $n_D^{25} = 1.4470$; 3) 165—170°, 9.6 g, $n_D^{25} = 1.4511$; 4) residue.

The main fraction 158—165° was of an unsaturated character, and in the same way as in the former paper this fraction (30.4 g) was subjected to hydrogenation over platinized charcoal at 170° in order to determine its chemical nature. The condensate (27.7 g) which was saturated had $n_D^{25} = 1.4302$. This condensate should have contained a certain amount of the unchanged menthane and therefore it was subjected to dehydrogenation over platinized charcoal at 300°. A condensate (25.8 g) was obtained that had a considerably higher refractive index: $n_D^{25} = 1.4455$. In order to eliminate *p*-cymene from the condensate, the latter was treated with an equal volume of fuming sulphuric acid containing 5% of $SO_3$. The remaining hydrocarbon was washed, dried and distilled over sodium. A hydrocarbon was obtained (17.4 g) that

had the following properties: b. p. 154.5—161.5°/746 mm; $n_D^{20} = 1.4301$; $d_4^{20} = 0.7830$; $MR_D = 46.25$; calculated for $C_{10}H_{20}$—46.18.

It may be seen from these constants that starting from menthene we had obtained through a series of contact transformation a final product consisting of a mixture of pentamethylene hydrocarbons $C_{10}H_{20}$ formed through the hydrogenation of cyclopentene hydrocarbons, $C_{10}H_{18}$. It is the latter that had been the immediate product of the contact isomerization of menthene. In a second experiment, after bringing 26.7 g of menthene twice in contact with silica gel at 400°, we isolated the main fraction 150—165° (23.4 g) having a refractive index $n_D^{20} = \mathbf{1.4510}$. This fraction (21.6 g) was hydrogenated over platinized charcoal at 165°. The condensate after the hydrogenation (20.4 g) had $n_D^{20} = 1.4349$. After the dehydrogenation over the same contact at 300°, 18.6 g of a product were obtained having $n_D^{20} = 1.4472$. The hydrocarbon remaining after the treatment of the condensate with fuming sulphuric acid was washed, dried and distilled over sodium. A hydrocarbon was obtained (11.8 g) having b. p. 157—162°/749 mm; $n_D^{20} = 1.4308$; $d_4^{20} = 0.7820$; $MR_D = 46.38$; calculated for $C_{10}H_{20}$—46.18.

Rupture of the Pentamethylene Cycle. After passing the product having a b. p. 157—162° twice over platinized silica gel at 300° at a rate of 5 drops per minute, a condensate was obtained that had $n_D^{21} = 1.4243$. This condensate was treated with fuming sulphuric acid in order to eliminate aromatic hydrocarbons that could have formed through contact with platinized silica gel. The residue was washed, dried and distilled over sodium: b. p. 144—161°/743 mm; $n_D^{20} = 1.4198$; $d_4^{20} = 0.7535$; $MR_D = 47.73$; calculated for $C_{10}H_{22}$—48.38.

Thus, through the hydrogenation of pentamethylene hydrocarbons $C_{10}H_{20}$ we obtained a mixture of isomeric decanes. A somewhat low molecular refraction may be explained by the fact that the rupture of cyclopentene hydrocarbons through hydrogenation was accompanied by a side process consisting of a further and deeper cleavage of the paraffinic hydrocarbons formed.

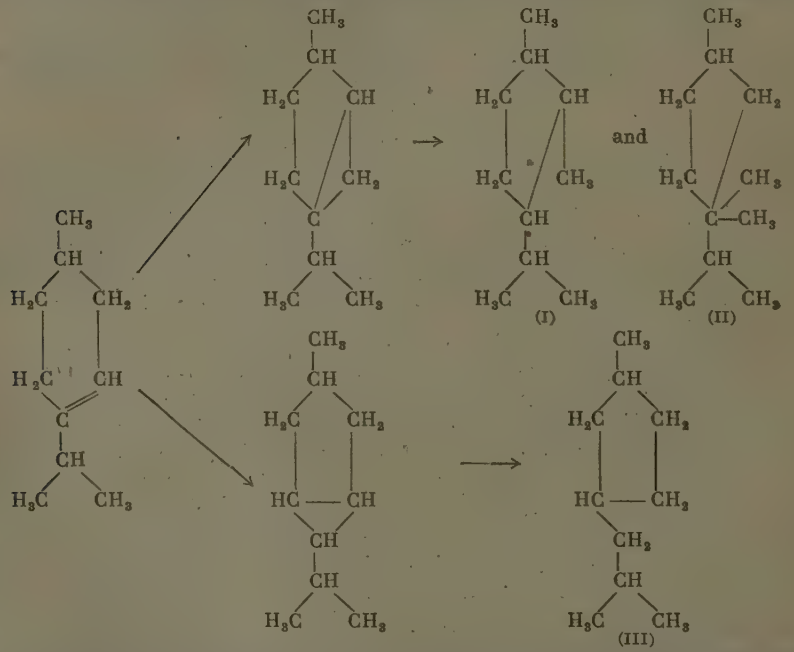
A third experiment on the contact transformation of menthene over silica gel was carried out at 450°. In this experiment after passing menthene (30.3g) twice over silica gel a condensate was obtained (25.6 g) which had $n_D^{21} = 1.4520$ and which was subjected to fractional distillation. The following fractions were collected: 1) up to 150°, 4.5 g, $n_D^{21} = 1.4439$; 2) 150—165°, 12.4 g, $n_D^{21} = \mathbf{1.4522}$; 3) 165—170°, 3.9 g, $n_D^{21} = 1.4611$; 4) a small residue. In this experiment the condensate distilled in a larger interval compared with experiments at 375 and 400°. In this case, besides the main fraction 150—165° there was a rather considerable amount of a lower boiling fraction.

Fraction 150—165° was hydrogenated over platinized charcoal. The product of hydrogenation (11.1 g) had $n_D^{20} = 1.4361$. After its dehydrogenation at 300° 10.8 g of a hydrocarbon were obtained, having $n_D^{20} = 1.4445$. After the elimination of cymene by treatment with fuming sulphuric acid, the remaining hydrocarbon (7.1 g) had: b. p. 155—162°/751 mm; $n_D^{20} = 1.4302$; $d_4^{20} = 0.7811$; $MR_D = 46.37$; calculated for $C_{10}H_{20}$—46.18. The constants of this product coincide nearly with those of the mixture of pentamethylene hydrocarbons, obtained in the experiments mentioned above.

The low boiling fraction (4.5 g) was also hydrogenated and the condensate had $n_D^{21} = 1.4291$. After the dehydrogenation of this condensate at 300° a product was obtained having $n_D^{20} = 1.4358$. The latter was treated with fuming sulphuric acid and the residue was washed, dried and distilled over sodium.

A hydrocarbon was obtained (1.5 g) which distilled below 150° and which had $n_D^{20} = 1.4214$. The data cited above leave no doubt about the fact that this product consisted mainly of a mixture of paraffine hydrocarbons.

Hence, when menthene was brought into contact with silica gel, next to its isomerization into cyclopentene hydrocarbons, a partial rupture of the unsaturated six-membered cycle took place with the formation of unsaturated acyclic hydrocarbons. As to the structure of the cyclopentene hydrocarbons $C_{10}H_{20}$ obtained from *p*-menthene-3 through a series of consecutive contact transformations, theoretically the formation of three isomeric saturated pentamethylene hydrocarbons (I, II, III) from menthene might be expected. As there is no doubt about the possibility of a shift of the double bond during the contact of menthene with silica gel at 375—450°, the formation of other isomeric pentamethylene hydrocarbons may also take place:




Out of these hydrocarbons only 1.2-dimethyl-3-isopropyl-cyclopentane[1] is described in the literature. It was obtained both synthetically [2] and through the contact hydrogenation of thuyene [3,4], thuyane [4], sabynene [5] and from the addition product of hydrogen bromide and thuyane [6].

1.2-dimethyl-3-isopropyl-cyclopentane, prepared by Kazansky through the catalytic decomposition of thuyane-menthylidene-hydrazine, had the following properties: b. p. 159—160.5°/757 mm; $n_D^{21} = 1.4328$; $d_4^{21} = 0.7877$.

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*CHEMISTRY*

# PRIMARY STAGES IN FORMATION OF BLACK PLATINUM

By D. L. BERDICHEVSKAJA and P. D. DANKOV

*(Communicated by Wl. A. Kistiakowsky, Member of the Academy, 25. VI. 1939)*

§ 1. Finding out the mechanism of the primary stages of formation of the dispersed metallic systems which form when the metals are reduced from solutions of their salts, is a problem of the origin of metallic crystals (1). Unlike usual crystallization processes the precipitation of the metal during reduction is associated with a well defined chemical change, corresponding to the passing of the metal ions into a crystalline state and the oxidation of the reducer. The processes which take place thereby are so complicated that at the present time the theory of the problem is in a rudimental state. The explanation of the phenomenon of metal formation by reduction is usually based on the formal ideas of competition between the velocities of formation and growth of the metal nuclei. However, such juxtapositions did not give a concrete picture of the formation and growth of the nucleus.

The application of Gibbs-Volmer's theory to the phenomena of the reduction of metals from solutions (2) was an essential step forward.

Development of the idea of the nucleus formation work and of the decrease in this work in the presence of the surface of solid bodies which have some relationship to the material which is crystallizing, made it possible for Volmer to indicate how to make the crystallization process easier in the presence of such surfaces.

In the phenomena accompanying the crystallization of liquids or salts from their solutions the importance of the presence of foreign surfaces as factors facilitating crystallization has been noted long ago (3) and is confirmed by modern data (4). The influence of dust particles which fell into the liquid from the air was noted most of all. How great is the importance of such particles for the formation of nuclei is evident from the work by Meyer and Pfaff (4) who, after carefully puring benzophenon of dust, could not crystallize it even at the temperature of liquid air (—183° C).

In the domain of phenomena of the formation of metallic particles which arise during reduction from solution, the influence of dust particles as factors which facilitate the formation of crystalline nuclei has not been examined.

§ 2. In this work we made a study of this problem in application to the reduction of platinum from alkali solutions of its salts with formaldehyde. For the purpose the chemically pure solutions of chloroplatinic acid, the alkali and the formaldehyde were carefully freed of dust. The water for the solutions was distilled twice in a still of Jena glass, where the bidistillate was completely isolated from the outside air; the flasks which were used as

receptors were first filled with dustless water and were freed from the latter in such a way that the water displacing the air could get into the flask only after filtration through Schott's small-pored filter. Only in this manner was it possible to keep the bidistillate coming from the still from the polluting action of dusty air which gets into the flask from the atmosphere.

The chemically pure solution of cloroplatinic acid (0.218 $N$) and sodium hydroxide (2.8%) were freed from dust by filtration into flasks filled with dustfree air. The formaldehyde solution (1.83%) was produced by immediate distillation of commercial formalin into flasks, free from dust. The absence of dust was established by observing Tyndal's cone from a bright light source.

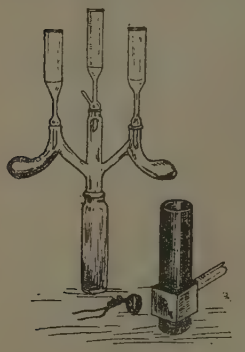

Fig. 1.

The reaction apparatus used in the experiments was a combination of three vessels connected to one another; funnels with small-pored Schott filters were put into opening in these vessels (Fig. 1). Before the experiment the air in it was also carefully cleared of dust. Then the chloroplatinic acid solution was filtered in the cylindrical part of the apparatus, while the alkali and formaldehyde solutions were filtered in two other flasks. Inclining the apparatus, the formaldehyde and alkali solutions were successively poured into cylindrical vessel whereupon observations were made.

Preliminary observations showed that purification of the solutions and the air above them from dust has an essential influence over the process of precipitation of metallic platinum by reduction. The distinction was especially notable during the induction period, which is characteristic for this kind of phenomena. During the experiment of reduction of the temperature of melting ice when the solution and the apparatus were isolated from dust, the process did not begin even in 420 min. after the reagents had been mixed, while when dusty air had free access the first stages of reduction were observed already in 60 min. A study of the reduction process at various concentrations of the reagents also showed the length of the induction period to vary with concentration.

In order to characterize these phenomena quantitatively we applied the method of measuring the «blackening» of the solution by means of a photoelement. For this purpose a light beam was passed through the solution and caught by a cupro-oxide photoelement connected to a sensitive galvanometer. The reaction vessel was placed in an ebonite cylinder (Fig. 1) which served to isolate the apparatus from foreign light sources. This method was used for an analogous purpose by A. Pospelov ([5]).

§ 3. As a result of the study it was established that in all cases of reduction of platinum from alkali solution by means of formaldehyde the metal always begins to precipitate after a certain induction period which increases: a) if the concentration of the reagents is decreased (Fig. 2), b) if the solutions are freed of dust (Fig. 2) and c) if the temperatures of the solutions are lowered.

§ 4. An analysis of the product shows that the velocity of the process of reduction of the metal is determined by the conditions of formation of the first portions of metallic phase. The formation of nuclei is here a difficult process, but after they have accumulated, reduction goes on very quickly (Fig. 2). Indeed, if we compare the time corresponding to the induction period with that of the reduction process, we become convinced (the table) that in the region of high concentrations, at a comparatively low stage of development of the reduction process corresponding to 6% reduced pla-

tinum, 47% of the time is spent in the induction period, while the rest of 53% is necessary to precipitate the main mass of the metal; at low concentrations the contrast is no less striking: 73% of the time goes for the formation of 19% of the metal, and only 27% for the precipitation of 81% of the metal.

From the table we also can see that lowering concentration of the reagents results at first in a small increase in the induction period, but afterwards a little change in the concentration provokes a sharp increase in the induction period.

| Concentration | 1 | 0.5 | 0.33 | 0.25 | 0.2 | 0.166* |
|---|---|---|---|---|---|---|
| Induction period | 14 | 34 | 42 | 76 | 88 | 180 |
| Duration of experiment | 30 | 50 | 60 | 95 | 120 | 215 |

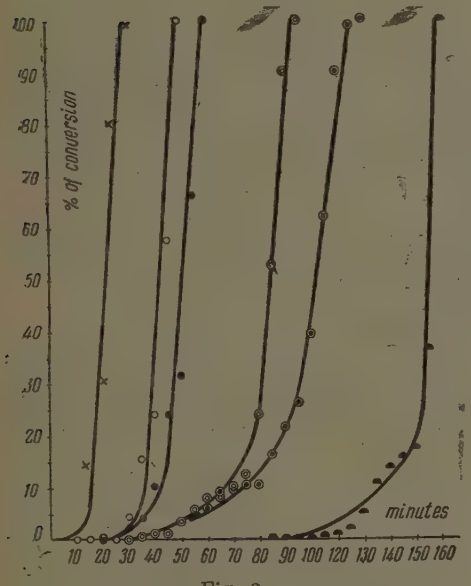


Fig. 2.

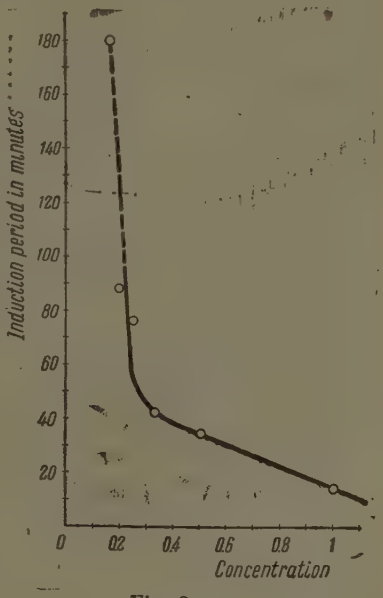


Fig. 3.

The latter circumstance can be illustrated in Fig. 3 which shows that the curve of induction periods in relation to the concentration has an inflexion in the region of concentrations, corresponding to app. 0.3 of the initial concentration of the reagents.

A comparison of this diagram with the data available on the exponential course of the curve of the formation of nuclei in various condensation and crystallization processes ([6]) permits us to conclude that Gibbs-Volmer's theoretical scheme is in principle applicable to the phenomenon of the reduction of platinum from its solutions.

The decrease in the induction period when the temperature is increased is evidently connected with the increase in activity of the reagents.

Finally, the presence of dust in the solution (Fig. 2) may be explained by the extraordinary difficulties met with in the formation of a nucleus in a homogeneous medium. The surfaces of dust particles serve as receivers for the precipitating metal atoms, and if they are given correct orientation they

* In this experiment the temperature was 27°, while in all other cases the measurements were taken at 29°.

facilitate the formation of the nucleus. Further growth of the nucleus apparently differs principally from its formation stage. It must be assumed that even when the solutions are freed from dust, very tiny particles stay in them, but since they are of extremely small size, the probability of a nucleus forming on them decreases.

§ 5. The conclusions to be drawn from the data obtained are as follows:

1. Platinum is reduced by formaldehyde from its alkali solutions in two sharply differing stages: the slow formation of nuclei (induction period) and the quick precipitation of metal in the presence of nuclei.

2. Decreasing the concentration of the reagents results in the increase of the induction period, and in the low concentration section there is an inflexion in the curve of induction periods which shows that in the region of low concentrations the stability of homogeneous solution sharply increases.

3. An increase in temperature decreases the induction period, which is connected with the change in the usual kinetic factors of chemical processes.

4. Removing the dust from the solution greatly decreases the induction period of reduction and checks the process altogether at low temperatures. This fundamental fact shows the tremendous importance of a solid body surface in the formation of nuclei when reducing a metal from solutions of its salts.

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*CHEMISTRY*

# CONTRIBUTION TO THE THEORY OF COMPLEX COMPOUNDS

By ANNA GELMAN

*(Communicated by N. S. Kurnakov, Member of the Academy, 15. VI. 1939)*

In studying ethylene compounds of platinum (1) we met with some very curious facts: first, the reactions

$$NH_4[PtC_2H_4Cl_3] + \underset{NCl+}{\overset{NH_3}{\rightleftarrows}} [PtNH_3C_2H_4Cl_2]$$

go on with the velocity of ionic reactions; secondly, as a result of the direct reaction we always obtained the dichloride of transconfiguration, whereas according to Peironnet's rule the cisform should have been expected.

In order to explain these facts it was necessary to make the assumption that ethylene possesses a high transinfluence in its inner sphere. This assumption, truly, seemed somewhat risky at first, since I. I. Černjaiev, in formulating the transinfluence law discovered by him in 1926 (2), considered only acid radicles transactive. It was known as an exception that thiourea shows a high transinfluence in comparison with acid radicles (3).

In a number of our next works we tried to confirm experimentally the idea of high transinfluence in ethylene. Fist of all, on the basis of this idea, we were successful in synthesizing the chloride $[PtC_2H_4ClNH_3Cl]$ of the cisform by acting with ethylene on Kossa's salt (4); this chloride differs sharply in properties from the chloride $[PtC_2H_4NH_3Cl_2]$ obtained from Zeise's salt.

Analogous compounds of the cis- and transforms were produced with propylene, styrole (5) and divinyle (6) and also with carbon monoxide (7) and nitric oxide (8). Finally, with the production of cis $[PtNH_3ClPyCl]$ (9) both by acting with pyridine on Kossa's ammonia salt, and by acting with ammonia on Kossa's pyridine salt the problem of the high transinfluence of unsaturated molecules received single valued solution.

The nature of the bond between ethylene and platinum has been discussed quite often in the last few years. The reason for the bond was sought either in the dipole moment which, by the way, equals 0, or in the formation of a solitary pair of electrons (10). In the latter case ethylene should have been joined co-ordinatively to the platinum at the expense of the unseparated pair of electrons in the first carbon atom, i. e. after the type of Sidgwick's ammonia addition (11); CO and NO addition should come about in a similar manner.

Although the analogy between the ethylene and ammonia compounds has been shown by many research workers, from Jörgensen (12) to Hückel (13),

Anderson [14], Bailar [15] etc., this purely external analogy consists only in the fact that ethylene, just as ammonia, takes up one co-ordinational place.

In a successive study of complex compounds of platinum and unsaturated molecules (l. c.) we were successful in observing a finer chemical behaviour in these compounds. First of all I have in view the high transactivity of ethylene hydrocarbon and unsaturated molecules in general. Where do they get this high transactivity? The question can by no means be solved if the approach to ethylene hydrocarbons CO and NO respecting their co-ordinational addition to platinum is by way of analogy with ammonia, and so they have been approached up till now.

I propose therefore considering unsaturated molecules not as donor groups any more, but as electron acceptors or, even better, as acceptors and donors at the same time.

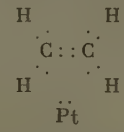
It is well known that electron structure of ethylene may be considered in two ways:

I II

In the free state ethylene is represented mostly by structure I, but if it comes into the sphere of action of c. a., it becomes excited and its structure becomes as II. Thus far our reasoning does not disagree with that of the authors referred to above. The disagreements begin later.

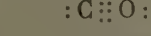
According to structure II, one carbon atom has a full octet of eight electrons, and the second two electrons missing. I consider that the second carbon atom can build up its octet at the expense of the two electrons given up by platinum (c. a.) for common use.

Being a donor, the platinum atom becomes a little more positively charged and can become an acceptor of the unseparated pair of electrons which was formed as a result of polarization, around the first carbon atom. All in all we have here a four-electron covalent bond. It is possible that this four-electron bond forms simply as a result of resonance according to the scheme

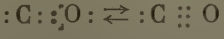


since the second pair of electrons which form the double bond in ethylene, is in a plane perpendicular to that in which the first pair of electrons are.

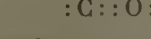
The following formula is generally accepted at the present time for the carbon oxide:



or, rather, the equilibrium of two conditions:



shifted towards the right. The third pair of electrons in common use is given only by oxygen forming a co-ordinational bond according to the scheme:



Thus, the carbon atom in carbon monoxide proves already to be an acceptor and therefore, when it comes into the sphere of action of the c. a., it is much

easier for it than for the carbon atom in ethylene to build up its octet at the expense of the electrons given by platinum. Again we get a covalent bond, formed of two pairs of electrons, just as in the case of ethylene addition:

$$Pt::C::O:$$

In structure, nitric oxide is very similar to carbon monoxide:

$$\cdot\ddot{N}::\ddot{O}: \rightleftarrows \cdot\ddot{N}:::O: \qquad \cdot\ddot{N}::\overset{\frown}{O}:$$

and forms the bond with the central atom in a similar manner.

But nitric oxide has one extra electron. It may be expected that it will enter fully into the disposal of the c. a.; as result of this the platinum atom becomes negatively charged and the nitrogen atom positively charged, and the electrostatic attraction between them adds to the covalent bond. This can probably explain the increase in co-ordinational durability of NO in comparison with CO and $C_2H_4$.

Thus, in forming complex compounds with unsaturated molecules platinum acts both as donor and acceptor at the same time.

However, at the expense of which electron does platinum become a donor? I think that these are the same electrons at whose expense platinum shows its quadrivalency.

It should be noted that according to both published data and our observations (the paper is being prepared for print) complex compounds with unsaturated molecules are formed only by bivalent platinum and in general by metals in the lowest stage of oxidation. The appearance of donor properties in the platinum and the formation of a four-electron covalent bond should at once have its effect on the fine chemism of the inner sphere, which we really observe in the form of high activity of the inner sphere—high transinfluence of the unsaturated molecules. From this point of view we can explain many facts that seemed incomprehensible up till now in the behaviour of complex compounds of platinum and unsaturated molecules.

1. If the unsaturated molecules have a great transinfluence, then two such molecules cannot be instilled in the complex (as is observed during the formation of complex compounds with thiourea), because the platinum atom has no more donoric ability.

2. Transactive unsaturated substitutes are easily displaced by an excess of ammonia or pyridine, i. e. possess less co-ordinational durability in comparison with them, because although the c. a. is a donor, the more advantageous configuration, in respect to energy, is produced when the platinum atom is acceptor.

3. The co-ordinational durability of hydrocarbon decreases according to the series:

$$C_8H_8 > C_2H_4 > C_2H_6 \sim C_4H_8$$

therefore it is evident that some of the radicles promote polarization of the double bond (the phenyl group), while the other check it, some strengthen the four-electron bond with the c. a. and the other weaken it.

One more problem is left for us to explain why does thiourea show a high transinfluence.

According to the nature of its structure thiourea can be only a donor, but unlike ammonia and pyridine it can give four electrons for common use:

$$Pt::S::C\begin{matrix}NH_2\\NH_2\end{matrix} \qquad Pt::S\begin{matrix}C_2H_5\\C_2H_5\end{matrix}$$

Such a bond immediately affects the chemical properties of the inner sphere and appears again in the form of high transinfluence. Unlike unsaturated molecules thiourea can enter into the complex in the quantity of two and three molecules, since co-ordinational addition comes about exclusively at its expense (just as in the case of ammonia, pyridine, etc.).

Thioethers, the thiosulphate ion etc. should behave just the same in platinum complexes. The difference may be only in details, as a result of the fact that the sulphur atom is joined to various atoms; consequently, the imposition of polarization, space and other phenomena is possible.

It may be assumed that when chlorplatinite is acted upon with thioether, the dichloride [Pt2 $(C_2H_5)_2SCl_2$] of the transform (α) is formed in the first place just as in the case of thiourea. Assuming a high transinfluence in thioether, we can expect that the cis (β) and trans (α) isomers should differ sharply in their chemical behaviour, as we have been able to observe on the example of ethylene and carbonyl platinum amindichlorides[4]. The cis-isomer (β) should behave almost as an electrolyte, which is borne out by experiment[16]. Its behaviour fits into Werner's co-ordination theory and all of Drew's and collaborators excogitated constructions with regard to the cis (β) isomer are entirely unnecessary.

The transinfluence law [2] developing Werner's doctrines not only shows the experimenter the correct way to reach the goal aimed at, but also explains the specific behaviour of various substitutes in the inner sphere, connected with their nature. It remains only to be regretted that foreign research workers, working on complex compound, do not give it enough attention.

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*CHEMISTRY*

# SURFACE STRUCTURE OF PASSIVE IRON

By P. D. DANKOV and N. A. SHISHAKOV

*(Communicated by Wl. A. Kistiakowsky, Member of the Academy, 13. VI. 1939)*

§ 1. The structure of a natural oxide film on iron, formed in air, has been studied rather elaborately (1). The same cannot be said of the artificial passivizing film which forms on iron when it is submerged in liquid oxidizing media (e. g. solutions of $K_2CrO_4$, $K_2Cr_2O_7$, $HNO_3$). The short article by Japanese authors (2) on the structure of the oxide film on iron, isolated after Evans' method, aroused doubts because of the possibility of destructing the initial film structure while isolating it and bombarding it with fast electrons. Evans' is a very elegant method but its drawback is that little reliance can be placed upon the initial film being able to retain its structure throughout the operations of isolating it. The influence of fast electrons on the structure of the film was not discussed in the Japanese authors' short article.

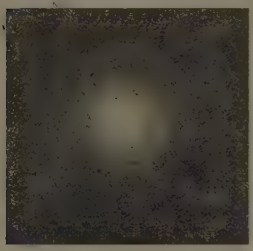
§ 2. In this work a new way of studying passivizing films was applied: very thin iron films were prepared on mica or glass by condensing the vapours of the metal in a vacuum. After having been brought into contat with the atmosphere, the metallic films were separated from the underlying material in the following manner. This material was submerged together with the film immediately in an oxidizing solution (a saturated solution of $K_2Cr_2O_7$, $^1/_{20}\,n$ solution of $K_2CrO_4$ or in strong nitric acid). After a short time the metal films exfoliated from the mica or glass and floated freely upon the surface of the liquid. The films were kept for various length of time upon the surface of the oxidizing solution, and then were quickly transferred on a platinum net to the surface of distilled water, where the oxidizing solution was washed from them.

The iron film samples with the passivizing oxide layers on them produced in this way were checked by comparison experiments in dissolving them in weak nitric acid. Here it was observed that those films which had been in contact only with air dissolved instantaneously leaving almost invisible films (apparently of oxide) on the surface of the acid solution. On the other hand, those iron films which had been subjected to the action of a passivizing agent (e. g., $K_2Cr_2O_7$, or concentrated $HNO_3$) for even a very short time, did not dissolve in the weak acid solution for an indefinitely long time.

After being washed in distilled water, the iron films with the passivizing oxide layers were fished out into a brass frame, whose opening had been preliminarily covered with a celluloid membrane. After a quick drying the samples were studied in the electronograph; the conditions under which work is done with the electronograph have been described before(1).

§ 3. The use of thin iron films as the bearers of the passivizing film made it possible for us to apply the method of passing electrons as the one which

gives the most accurate data. In using this method we did not measure the accelerating tension; the doubled product ($2\lambda L$) of the electron wave length ($\lambda$) and the effective length of the electronograph ($L$) which is needed in the calculations, was obtained from the data for iron lines which were nearly always present in the sample, and from available accurate X-ray data on the constant ($a$) of the iron lattice. The calculations were made according to the usual formula:



$$a = 2\lambda L \frac{\sqrt{h^2 + k^2 + l^2}}{D},$$

where $h$, $k$ and $l$ are values proportional to Miller's indices and $D$, the measured diameter of the diffraction ring.

§ 4. A number of samples passivized in a saturated solution of potassium bichromate or in concentrated nitric acid were subjected to electronographic analysis. The electronograms were identical for all the samples. We give a typical electronogram in Fig. 1. In Table 1 we compare the results of measurements and calculations made for this electronogram. The diameters of the rings were measured independently by both of the authors with accurate rules and magnifying glasses which magnified five times, and also with a Zeiss comparator which magnified 15 times. The accuracy of the measurements fluctuated from 1 to 0.2%. The average accuracy ranged between 0.3 and 0.6%.

Table 1

| Intensity | Diameter of rings in mm | Phase | Indices | $2\lambda L$ ($a$=2.861 Å) | Constant of oxide lattice in Å |
|---|---|---|---|---|---|
| Very strong, wide . . . | 12.1 | oxide | 113 | | Indef. |
| Very strong . . . . . | $15.0_3$ | α-iron | 110 | 30.51 | |
| » wide . . . . . | $21.0_0$ | oxide | 440 | | 8.22 |
| » » . . . . . | $26.1_2$ | α-iron | 112 | 30.51 | |
| Medium, wide . . . . . | $29.9_5$ | oxide | 800 | | 8.15 |
| Medium . . . . . | $33.6_0$ | α-iron | 310 | 30.40 | |
| Small, wide . . . . . | $35.5_4$ | oxide | 844 | | 8.18 |
| Strong . . . . . | $39.8_6$ | α-iron | 321 | 30.48 | |
| Medium . . . . . | $45.5_3$ | » | 330 | 30.70 | |
| | | | Average | 30.52 | 8.18 |

After 8 electronograms had been measured, the average value of the oxide lattice constant was calculated: $a = 8.17 \pm 0.05$ Å. The corresponding X-ray value for $\gamma$-$Fe_2O_3$ is considerably greater ($a$=8.32 Å).

Thus, in comparison with α-iron ($a$=2.861 Å) the crystal lattice of the oxide ($\gamma$-$Fe_2O_3$) is compact. However, on the basis of Riedmiller's data [3] for nickel it may have been expected that the iron lattice constant would be increased for thin layers. In order to check this circumstance the iron lines were compared with kaolin lines, for which one of the authors (N. A. Shishakov) was able to obtain accurate electronographic data. For this purpose a thin layer of kaolin was deposited upon one of the studied samples (from an aqueous suspension), i. e. samples with three layers: iron, oxide and kaolin, were produced. The results of an electronographic study of this sample are given in Table 2.

Table 2

| Intensity | Diameter of rings in mm | Phase | Indices | $2\lambda L$ ($a$=2.861 Å) | Constant of oxide lattice in Å |
|---|---|---|---|---|---|
| Very strong, wide . . . | 7.2 | Kaolin | 100 | Indef. | |
| » » . . . . . | 12.1 | » | 110 | 31.22 | |
| » » . . . . . | $15.1_7$ | Iron | 110 | | $2.89_9$ |
| Medium . . . . . | $18.4_5$ | Kaolin | 210 | 31.16 | |
| Very strong . . . . . | 20.8 | » | 300 | 30.97 | |
| Medium . . . . . | 24.0 | » | 220 | 30.97 | |
| » . . . . . | 25.0 | » | 310 | 31.00 | |
| » . . . . . | $26.2_5$ | Iron | 112 | | $2.90_1$ |
| Weak . . . . . | 30.2 | Kaolin | 400 | 31.03 | |
| » . . . . . | 32.2 | » | 320 | 31.30 | |
| » . . . . . | 34.0 | Iron | 310 | | $2.89_2$ |
| | | | Average | 31.09 | $2.89_7$ |

From Table 2 it is evident that the constant calculated for the lattice ($a$=2.897) is app. 1.3% greater than for normal iron ($a$=2.861 Å). For the other samples the difference is app. 1.9%. On the average it may be assumed that in the cases examined the iron lattice expands app. 1.5%.

Therefore the calculations of the iron oxide lattice constant given above should be corrected in accordance with the calculated value of the lattice constant of iron which served as the standard substance. Calculation shows that the corrected value of the lattice constant of the cubic oxide is higher, viz. $a=8.29\pm0.05$ Å. This value is close enough to the constant value for $\gamma$-$Fe_2O_3$ ($a$=8.32 Å). Thus, the passivizing oxide film is made up of extremely thin crystals of cubic iron oxide ($\gamma$-$Fe_2O_3$).

§ 5. The results of this study show that the passivizing film on the iron consists of a thin layer of the small grained oxide ($\gamma$-$Fe_2O_3$). The simple operations of transferring the samples from the oxidizing solution into the frame could not have caused essential changes in the structure of the passivizing film. On the other hand, with the conditions in which the electronograph has operated in the experiment, the distorting action of the fast electron bombardment was unnoticeable even in the case of such comparatively unstable compounds as iron hydroxide, which are also studied in our laboratory. Therefore the data given above should be referred to the passivizing oxide film which formed initially on the surface of the iron. At the end of this study we were able to become acquainted with Finch's publication ([4]) on the structure of the passivizing oxide film on iron. To Finch's opinion the oxide film is in an amorphous state. It is hardly possible to agree with this conclusion not only because of the contradictions between our results and Finch's assertions, but also on account of the lack of clearness as to the conditions of his experiments which tend to obscure the general picture.

Of course, there is a possibility that there may be an amorphous component of the oxide in the film which under suitable conditions, e. g. in Finch's experiments, may have become predominant.

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*CHEMISTRY*

# DETERMINING THE COMPOSITION OF SOLID PHASES OF EQUILIBROUS QUADRUPLE SYSTEMS

By V. I. NIKOLAEV

*(Communicated by N. S. Kurnakov, Member of the Academy, 25. VI. 1939)*

The possibility of applying Schreinemakers' method to determining the composition of solid phases in multicomponent systems has already been proven by F. M. Perelman (1). In this report I shall show how to apply Schreinemakers' method in quadruple systems, represented in 60° co-ordinates, as proposed by me in 1936 (2).

The system taken for study was the quadruple aqueous mutual system $Na_2Cl_2+MgSO_4 \leftrightarrows Na_2SO_4+MgCl_2$ (25%), in which there are no solid solutions, but joint crystallization of two and tree salts may be observed, and which contains a double salt—astrakhanite.

Adding arbitrary quantities of one, two or three salts with which the liquid phase is in equlibrium, to the composition of the liquid phase at the moment of equlibrium, we will be able by means of simple calculation to find an intermediate point which corresponds to the composition made up of the liquid phase and the solid phases, and to mark both the direction of Schreinemakers' ray and the solid phase composition point of either one or two or three heterogeneous solid phases.

On the drawing (Fig. 1) we see 3 equilateral triangles adjoining each other and forming part of a rectilinear hexagon with a $H_2O$ point at the centre. Only three triangles forming a trapezoid are thus enough for the quadruple system. 4 co-ordinates are used to calculate the composition of liquid and solid phase: $H_2O$—$MgSO_4$; $H_2O$—$MgCl_2$; $H_2O$—NaCl and $H_2O$—$Na_2SO_4$.

In the calculations the motion is along a spiral. As I have already mentioned in a previous work(2), this method is a particular case of the more general method of spiral co-ordinates, proposed by V. Anosov.

In the triple system bounding on the quadruple system the composition of the solid phase is determined in the usual manner, i. e. Schreinemakers' ray is directed towards the composition point of the solid phase. Thus, from point *a* which is situated on the crystallization line of NaCl in the system NaCl—$MgCl_2$—$H_2O$, the ray is directed towards the vertex of NaCl (Fig. 1). From point *b* which is situated on the crystallization line of $MgSO_4 \cdot 7$ aq. in the system $MgSO_4$—$MgCl_2$—$H_2O$, the ray ends at the composition point of $MgSO_4 \cdot 7$ aq. In the same manner the ray from point *c* which is situated on the crystallization line of $NaSO_4 \cdot 10$ aq. of the system $H_2O$—NaCl—$Na_2SO_4$, ends at the composition point of $NaSO_4 \cdot 10$ aq.

In the quadruple mutual system $Na_2Cl_4+MgSO_4 \leftrightarrows Na_2SO_4+MgCl_2$ Schreinemakers' method makes it possible to determine also the composition of

two and even three solid phases which are in equilibrium with the liquid phase.

Thus, the ray coming from point *xy* of N. S. Kurnakov and S. F. Zhemchuzhny's diagram ends on the composition line of the hard phases $NaCl + Na_2SO_4$ (anhyd.).

The ray coming from point *d* which is situated on the line of joint crystallization of $NaCl + Na_2SO_4$, also ends at the $NaCl—Na_2SO_4$ side. Both mentioned rays intersect along their paths the composition line of $NaCl—Na_2SO_4 \cdot 10$ aq., which shows that the second solid phase (besides NaCl) is none other than $Na_2SO_4$ and not Glauber's salt $Na_2SO_4$. 10 aq*. Here the segments on the composition lines of $NaCl—Na_2SO_4$ make it possible to tell in what quan-

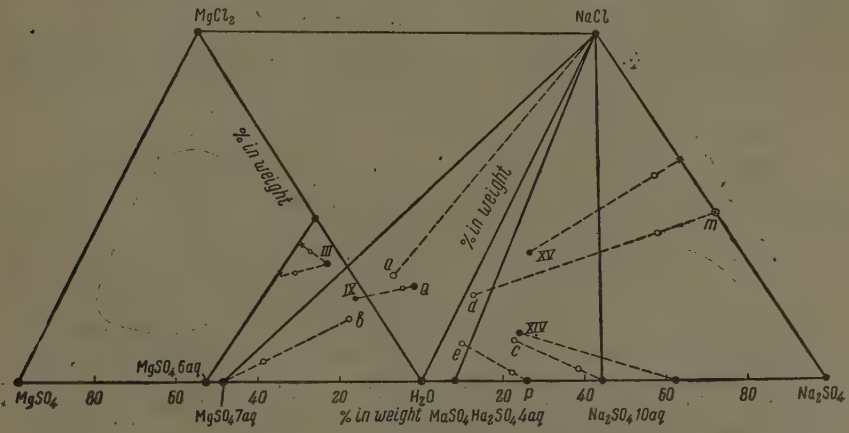


Fig. 1.

titative ratios the two solid phases in equilibrium with the liquid phase are present.

Thus, NaCl and $Na_2SO_4$ are present in equal quantities by weight at point *m* and these quantities are in equlibrium with the liquid phase of the composition of point *d*.

In the same manner Schreinemakers' ray coming from point *XIV* (N. S. Kurnakov's and S. F. Zhemchuzhny's diagrams) ends at point *n* which is situated on the composition line of $Na_2SO_4 \cdot 10$ aq.; this shows that the two solid phases are none other than $Na_2SO_4$ and Glauber's salt, and in quantities determined by the segments $n—Na_2SO_4$ and $n—Na_2SO_4$. 10 aq.

The ray coming from point *e* which is situated on the line of joint crystallization of astrakhanite and Glauber's salt, ends exactly on the composition line of the two solid phases mentioned above, at point *p*, which gives no grounds to tell in what weight ratios the two solid phases in question are present [segments ($Na_2SO_4$. $MgSO_4$. 4 aq.—*p*) and ($Na_2SO_4$. 10 aq.—*p*)].

Rays coming from point *III* end on the composition lines of the two solid phases $MgSO_4$. 6 aq. and $MgCl_2$. 6 aq., which proves the presence of these two salts in equilibrium with the liquid phase of the composition of point *III*.

It is possible also to determine the composition of three co-existing solid phases. The composition of the three solid phases at the famous *IX* point is determined by point *Q* which lies within the triangle $H_2O—MgCl_2—NaCl$

* The accuracy of determination of the composition of the solid phases evidently depends on the proximity of intermediate point to the line $NaCl—Na_2SO_4$.

between the composition lines of the solid phases: astrakhanite+NaCl and NaCl+$MgSO_4 \cdot 7$ aq. The fact that point $Q$ is situated between these two composition lines shows that there should be three solid phases simultaneously in the solid phases: NaCl+$MgSO_4$. 7 aq+$Na_2SO_4 \cdot MgSO_4 \cdot 4$ aq.

Thus, the composition point of three solid phases lies not on a line, but on an area between the composition lines of two solid phases.

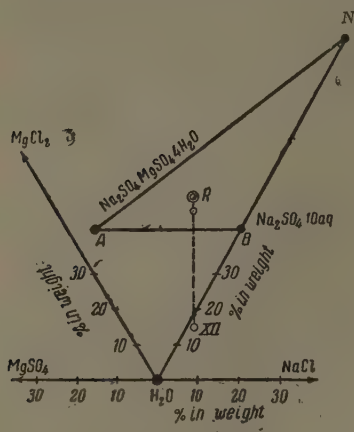


Fig. 2.

In the same manner, after changing the construction a little, we determine the composition of the three co-existing solid phases of astrakhanite, Glauber's salt and tenardite.

The composition of three solid phases is determined by a point lying in the area between two composition lines of two solid phases one of which should be common for both lines, or in the area between three composition lines, in which there are three different solid phases. In view of this fact the corner points in Fig. 1 NaCl and $Na_2SO_4$ have been transposed to Fig. 2.

As a result of this transposition it becomes possible to construct the triangle $ABC$ within which the composition of three solid phases should be found. Schreinemakers' ray drawn from point $XII$ ends at point $R$, lying within triangle $ABC$ which is formed of three lines: 1) line of astrakhanite+ +tenardite; 2) line of astrakhanite+Glauber's salt and 3) line of Glauber's salt+tenardite. Thus, the composition of the three solid phases in equilibrium with the liquid phase at point $XII$ is determined as: astrakhanite+ +Glauber's salt+tenardite.

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*CHEMISTRY*

# A STUDY OF COMPLEX COMPOUNDS OF PLATINUM AND COMPLEX AMINES

By A. M. RUBINSTEIN

*(Communicated by N. S. Kurnakov, Member of the Academy, 22. VI. 1939)*

Previous studies of pyridine and amino-pyridine complex platinum compounds brought us to the establishment of new types of complex compounds, and also permitted us to make mention of a few laws in the formation of complex compounds.

In the last paper on amino-pyridine complex platinum compounds we showed that amino-pyridine forms a complex compound with platinum with a cisconfiguration, viz. 2 am $PyCl_2Pt$.

It was of great interest to trace the variations in the properties of the complex compound in relation with the complexity of the amine, and also to find out how the size of the amine molecule influences the formation of complex compounds. Up till now in forming pyridine and amino-pyridine complex compounds the molecules were connected through the tertiary nitrogen. It was interesting to find out how the platinum would be connected in the complex compound if there were a haloid sibstituted pyridine ring. For this purpose we undertook a study of complex compounds of platinum and 5I·2 am Py. The difficulty of this work consisted in the fact that 5I·2 am Py is insoluble in water, for this reason it would be necessary to conduct all the reactions in alcohol-aqueous solution. 5I·2 am Py is quite soluble in alcohol, and is precipitated out again upon being diluted with water. Therefore the study of the complex compounds had to be conducted in an accurate concentration of alcohol and water in order that 5I·2 am Py should not be precipitated during the reaction.

A study of the interaction between iodo-amino-pyridine and potassium chlorplatinite showed that: 1) The reaction does not come about at once, a green precipitate begins to fall out not until several hours, and continues to fall out for quite a long time. 2) An analysis of the green precipitate showed that during this reaction a substance of the composition 2 (5I·2 am Py) $Cl_2Pt$ is precipitated according to the reaction

$$K_2PtCl_4 + 2\,(5I\cdot 2\text{ am Py}) = 2\,(5I\cdot 2\text{ am Py})Cl_2Pt + 2KCl.$$

The reaction was conducted with an exact theoretical quantity of iodo-amino-pyridine—2 molecules to 1 molecule of potassium chlorplatinite. 3) In forming complex compounds, iodo-amino-pyridine does not form complex compounds and takes up one co-ordination locus in the internal sphere of the complex compound. In order to find the properties of this complex com-

pound the action of pyridine and ammonia on 2 (5I·2 am Py) $Cl_2Pt$ was studied.

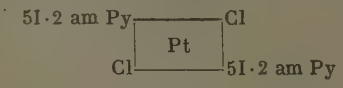
Action of Pyridine on 2 (5I·2 am Py) $Cl_2Pt$. The produced salt 2 (5I·2 am Py)$Cl_2Pt$ was dissolved in a small quantity of pyridine in the cold, and gave a solution of a dark brown colour. While this solution is left standing in the cold, there is no noticeable reaction; only after it has been heated over a water-bath for 30 min.—1 hour, there begins to appear a precipitate whose quantity does not increase upon further heating. The precipitate is filtered and washed with alcohol. The colour of the precipitate is yellow. Analysis of this substance shows that here we have the compound $Py_2Cl_2Pt$. This compound is produced according to the following reaction:

$$2\,(5I\cdot2\text{ am Py})Cl_2Pt + Py_2 = Py_2Cl_2Pt + 2\,(5I\cdot2\text{ am Py}).$$

That the reaction takes this course can be proved by the fact that iodo-amino-pyridine can be observed in the filtrate from $Py_2Cl_2Pt$; this iodo-amino-pyridine can even be extracted; for this purpose the filtrate is evaporated, diluted with a small quantity of alcohol, and then with water; when this is done, thin scales of iodo-amino-pyridine which is insoluble in water precipitate.

In order to establish the geometric structure of $Py_2Cl_2Pt$ and the 2 (5I·2 am Py)$Cl_2Pt$, we studied the action of thiourea on $Py_2Cl_2Pt$.

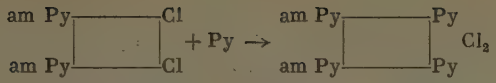
The salt $Py_2Cl_2Pt$ was heated over a water-bath with thiourea until the precipitate dissolved completely (the quantity of thiourea taken was exactly 4 molecules to 1 molecule of $Py_2Cl_2Pt$). The solution was acidified with a few drops of hydrochloric acid, and after a little while a snow-white large grained precipitate appeared. An analysis showed that when this is done, we get the compound [2 Th $Py_2$ Pt] $Cl_2$. According to N. S. Kurnakov's rules, the fact that such a compound is produced can be explained by a transconfiguration in our salt $Py_2Cl_2Pt$. Since this salt was obtained from 2 (5I·2 am Py)$Cl_2Pt$ by acting on it with pyridine, we can take it for granted that the compound 2 (5I·2 am Py)$Cl_2Pt$ also has a transconfiguration:




About 10 experiments were performed on the action of thiourea on $Py_2Cl_2Pt$, and the same results were obtained each time.

This result is of great interest, since this is the first time that a trans-salt has been observed to be produced by the action of pyridine derivatives on salts of bivalent platinum. This phenomenon can be explained only if we take it for granted that 5I·2 am Py is joined to the platinum through the iodine and not the tertiary nitrogen.

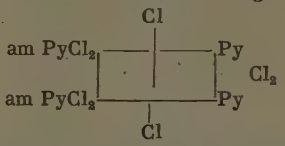
In order to show the difference in properties of the amine which is linked with platinum through its nitrogen and the iodized amine, we decided to perform an experiment of the action of pyridine on 2 am $PyCl_2Pt$ which has a cisconfiguration, and amino-pyridine is linked with platinum through its tertiary nitrogen. If the properties of iodo-amino-pyridine and amino-pyridine in these complex compounds are different, the correctness of our assumption on the bond between iodine and platinum will be confirmed. The study of the action of pyridine on 2 am Py $Cl_2$ Pt, produced by the action of alpha-amino-pyridine on potassium chlorplatinite, showed: 1) pyridine does not displace amino-pyridine; 2) when 2 am Py $Cl_2$ Pt is acted upon with pyridine, a tetramine is formed according to a reaction which agrees with Jörgensen's rule:




An aliquot of 2 am $PyCl_2Pt$ is dissolved in pyridine and heated over a water-bath; after a few minutes a precipitate appears, the latter is filtered off and washed with a small quantity of alcohol. After being well washed with alcohol, the salt is absolutely white. The salt is well soluble in water and alcohol, gives a precipitate of silver chloride in the cold with silver nitrate. Analysis for platinum, nitrogen and chlorine fully confirms the fact that the compound has the composition 2 am Py $Py_2$ Pt $Cl_2$. When this compound is acted upon with potassium chlorplatinite, there appears a greyish-pink precipitate according to the reaction:

$$2\ \text{am}\ PyPy_2PtCl_2 + K_2PtCl_4 \rightarrow [2\ \text{am}\ PyPy_2Pt]\,[PtCl_4].$$

A study of the oxidation reaction of 2 am $PyPy_2PtCl_2$ showed that in this case just as during the oxidation of 2 am $PyCl_2Pt$, besides platinum being oxidized, amino-pyridine is haloidized, forming the compound:

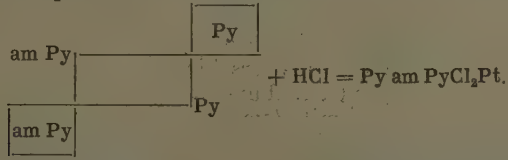



A red-coloured salt insoluble in water is produced immediately when gaseous chlorine is passed through a solution of the salt 2 am $PyPy_2Pt\ Cl_2$.

A determination of the electroconductivity of 2 am $PyPy_2PtCl_2$ also confirms the fact that we have in this case a tetramine:

| $\nu$ | 1000 | 2000 | 4000 | 8000 |
|---|---|---|---|---|
| $\mu_\nu$ | 216.0 | 220.0 | 224.8 | 227 |

A study of the action of concentrated hydrochloric acid on the tetramine 2 am Py $Py_2$ Pt $Cl_2$ showed that the compound is split according to Jörgensen's rule, and one molecule of pyridine and one of amino-pyridine are split off simultaneously, forming the mixed compound Py am Py $Cl_2$ Pt. The mixed chloride was obtained in the following manner: if a solution of the tetramine is treated with concentrated hydrochloric acid, a precipitate does not appear at once, and a yellow precipitate appears only after prolonged heating; according to an analysis for platinum, nitrogen and chlorine, this precipitate has the composition amPy Py $Cl_2$ Pt. The action of hydrochloric acid on the tetramine can be represented as follows:




As is evident from the above, the action of pyridine on 2 (5I·2 am $PyCl_2$ Pt) differs sharply from the action of pyridine on 2 am Py $Cl_2$ Pt. In the compound 2 (5I·2 am $PyCl_2Pt$) we have apparently a new type of bond which is accomplished by means of a haloid and not tertiary nitrogen.

At present supplementary experiments are being performed on studying the action of chloro- and bromo-amino-pyridines on platinum, which should confirm the correctness of our propositions.

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# ÜBER DIE CHEMIE DER EDELGASE. IV. MISCHKRISTALLBILDUNG ZWISCHEN EDELGASEN UND ANDEREN STOFFEN

Von B. A. NIKITIN

*(Vorgelegt von V. G. Chlopin, Mitglied der Akademie, d. 21. VI. 1939)*

In den früheren Mitteilungen(1) wurde am Beispiel der Molekül kristallhydrate nachgewiesen, dass die Edelgase hinsichtlich der Bildung von Molekülverbindungen zahlreiche Analoga unter den anderen Stoffen besitzen In der Tat besitzen die Kristalhydrate der Edelgase nicht nur dieselbe Zusammensetzung und denselben Bau wie andere Molekülkristallhydrate, sondern bilden mit diesen Mischkristalle.

Die Hydrate des Rn, Ar und Ne bilden Mischkristalle selbst mit Hydraten solcher Stoffe, deren Moleküle aus mehreren Atomen bestehen und ein permanentes Dipolmoment besitzen (so z. B. $SO_2$). Von diesem Standpunkt aus war es interessant festzustellen, wie weit diese Analogie geht und mit welchen Stoffen die Edelgase selbst als Mischkristalle auszukristallisieren vermögen. Von dem Hydridverschiebungssatz ausgehend, wies Grimm(2) darauf hin, dass die flüchtigen Hydride, die kein permanentes Dipolmoment besitzen, in manchen ihrer physikalischen Eigenschaften den Edelgasen sehr nahe stehen. Wie bekannt, nehmen die Wasserstoffatome oder die Protone in dem Kristallgitter keinen bestimmten Platz ein. Die Moleküle der flüchtigen Hydride verhalten sich wie Pseudoatome. Infolgedessen könnte man die Bildung von Mischkristallen zwischen $CH_4$ und Argon oder Krypton erwarten. Stackelberg, Quatram und Antweiler(3), sowie von Weith und Schroeder(4), haben dies an Hand von Erstarrungskurven experimentell festgestellt. Ungelöst bleibt jedoch die Frage, ob Edelgase mit flüchtigen Hydriden, die ein grosses Dipolmoment besitzen ($H_2S$, HCl, HBr, $NH_3$, $H_2O$) Mischkristalle bilden können. Die Dipolnatur der Moleküle äussert sich nur in der Struktur der Kristallgitter von $NH_3$ und $H_2O$. Ausserdem besitzen die Moleküle dieser Stoffe einen wesentlich kleineren Radius als die Atome des Ar und Rn. Die Kristallstruktur von $H_2S$, HCl und HBr hingegen ist von derselben Art wie die der Edelgase und ihre Radien nähern sich denjenigen der Atome schwerer Edelgase(5). Es gibt jedoch einige Hinweise auf Fälle von Mischristallbildung bei Stoffen, deren Moleküle aus verschiedener Anzahl von Atomen bestehen—so z. B. $Cl_2$ und $SO_2$ (6) oder HCl und $C_2H_6$(7). Bekannt ist auch ein Fall, wo ein Edelgas—das Argon—mit dem Sauerstoff Mischkristalle bildet(4). Die Erforschung der Möglichkeit der Mischkristallbildung zwischen den Edelgasen und den ihnen auf den ersten Blick durchaus unähnlichen Stoffen bietet deshalb ein bedeutendes Interesse.

Versuche wurden in der Hauptsache mit Radon, sowie z. T. mit Argon und Neon vorgenommen. Die Mischkristallbildung wurde nach den Methoden der Mitfällung und der Umkristallisation untersucht. Bei den Versuchen nach der Methode der Mitfällung wurden zuerst in einer U-förmigen im Kryostat bei niedriger Temperatur sich befindenden Röhre (von 50 ml Inhalt) Edelgase hineingelassen (1 ml Luft der gegen $10^{-12}$ g Rn enthält oder 1 ml Ar und Ne). Danach liess man sehr langsam das zweite Gas im Überschuss einströmen.

e Versuchstemperatur und die Einstromungsgeschwindigkeit des Gases rden so gewählt, dass die Kristallisation der flüssigen Phase umge- nd, unmittelbar aus der Gasphase stattfand. Nach Abschluss der Kristal- ation wurden die Edelgase sowohl in den Kristallen als auch in der sphase bestimmt.

Blindversuche zeigten, dass bei niedrigen Temperaturen an den Glaswan- ngen keine merkliche Adsorption der Edelgase stattfand. Unter den Ver- hsbedingungen blieben sie selbst in gasförmigem Zustande erhalten. Die Radon gewonnenen Ergebnisse sind in Tabelle 1 zusammengestellt.

Tabelle. 1

| Gas | Versuchs-temperatur | Gasdruck, mm | Ausgesch. ml Gas | Ausgeschie-den Rn in % | Ausscheidungs-geschwindigkeit |
|---|---|---|---|---|---|
| $NH_3$ | —136 | <0.1 | 1000 | 0.7 | 1 St. |
| HCl | —136 | 12 | 1000 | 81.2 | 1 » |
| » | —136 | 12 | 93 | 34 | 1 St. 20 Min. |
| $H_2S$ | —110 | 21 | 1000 | 98.4 | 1 » |
| » | —110 | 21 | 95 | 65 | 35 Min. |
| $SO_2$ | —110 | 0.2 | 1000 | 71.0 | 1 St. |
| » | — 90 | 2 | 100 | 20 | 1 St. 15 Min. |
| $CO_2$ | —110 | 35.7 | 1000 | 19.2 | 1 » |

r bei $NH_3$ ist die Aufnahme des Radons höchst gering. Die Ausscheidungs- chwindigkeit spielt eine bedeutende Rolle, da in diesen Versuchen die steme sich nicht im Gleichgewicht befanden. In den Versuchen nach der thode der Umkristallisation wurde Radon in eine Röhre hineingelassen, feine Kriställchen verschiedener Stoffe enthielt. Diese Röhre wurde wäh- d verschiedener Zeitdauer ausgehalten, wobei die Aufnahme des Radons olge der Umkristallisation des Stoffes stattfand (Tabelle 2).

Tabelle 2

| Stoff | Versuchs-temperatur, °C | Dampfdruck des Stoffes, mm | Stoffmenge | Ausgesch. Rn in % | Dauer der Umkristalli-sation |
|---|---|---|---|---|---|
| $H_2O$ | — 10 | 1.9 | 30 g | <0.1 | 2 Tage |
| » | —110 | ? | 3 » | <0.1 | 2 St. |
| $NH_3$ | —110 | 0.7 | 1000 ml | <0.1 | » » |
| $_6H_5OH$ | —130 | ? | 3 g | 0.7 | » » |
| $_5H_5NH_2$ | —110 | ? | 3 » | 0.3 | » » |
| HCl | —136 | 12 | 100 ml | 20.2 | » » |
| HBr | — 96 | 124 | 100 » | 25.3 | » » |
| $H_2S$ | —110 | 21 | 1000 » | 56.0 | 30 Min. |
| » | —110 | 21 | » | 80.5 | 2 St. |
| » | —110 | 55 | 47 » | 37.0 | 5 » |
| $SO_2$ | —110 | 0.2 | 1000 » | 3.6 | 5 Min. |
| » | —110 | 0.2 | » | 21.5 | 30 » |
| » | —110 | 0.2 | » | 39.0 | 2 St. |
| $CO_2$ | —110 | 35.7 | » » | 14.8 | 2 » |
| $_3COCH_3$ | —110 | ? | 3 g | 94.8 | 2 » |

Wie aus Tabelle 2 ersichtlich, wird das Radon von den Kristallen $H_2O$, $_3$, $C_6H_5OH$, $C_6H_5NH_2$ praktisch nicht mitgerissen. Dagegen wird es von Kristallen HCl, HBr, $H_2S$, $SO_2$, $CO_2$ und $CH_3COCH_3$ in erheblicher nge aufgenommen. Die Menge des aufgenommenen Radons nimmt mit Zeit stark zu, woraus zu ersehen ist, dass auch hier die Mischkristalle n mit der Gasphase nicht im Gleichgewicht befinden. Blindversuche zeig- , dass Anwesenheit von $CO_2$ in der Gasphase die Menge des vom Schwefel- xyd aufgenommenen Radons nicht vermindert. Wenn wir aber mit der

Adsorption des Radons an Silicagel zu tun haben, so wird die Menge des adsorbierten Radons durch die Anwesenheit von $CO_2$ um vielfaches vermindert [8]. Also kann das Mitreissen des Radons nur infolge der Mischkristallbildung geschehen. Es sei hier betont, dass sich die aus dem Koeffizienten der inneren Reibung berechneten Radien der Moleküle von $CO_2$ oder Aceton, von dem Radius des Radonatoms weniger als um 20% unterscheiden.

Mit Chlorwasserstoff scheidet sich eine merkliche, wenn auch nicht zu grosse Menge von Argon aus, wogegen es sich mit $NH_3$ gar nicht ausscheidet. Auch bei der Umkristallisation feiner Eiskristalle wird es nicht aufgenommen. Neon scheidet sich weder mit $NH_3$ noch mit HCl aus, noch wird es von den sich aus den Wasserdämpfen auf einer bis—185°C abgekühlten Oberfläche ausscheidenden Eiskristallen mitgefällt.

Die Methode der Mitausscheidung und der Umkristallisation hat aber den

Tabelle 3

Mitfällung von Ar und Ne bei Kristallisation von $NH_3$ und HCl

| Gas | Versuchstemperatur | Ausgesch. Menge des Gases, l | Ausgeschieden Ar in % | Ausgeschieden Ne in % |
|---|---|---|---|---|
| $NH_3$ | —185 | 1 | <0.1 | <0.1 |
| HCl | —140 | 1 | 1.0 | <0.05 |
| HCl | —160 | 2 | 2.5 | <0.05 |
| HCl | —185 | 1 | 3.1 | <0.05 |

Nachteil, dass sie keine Lösung der Frage gibt ob wir es mit einer lückenlosen Reihe von Mischkristallen zu tun haben, oder ob die Kristalle der zu untersuchenden Stoffe nur eine geringe isomorphe Beimishung von Edelgasen (gleich dem System $Cl_2$—$SO_2$) enthalten können. Ihr wesentlicher Vorteil besteht aber darin, dass sie die quantitative Trennung der Edelgase voneinander auf neue Art gestatten. So wird, z. B., durch die Mitauscheidung mit HCl bzw. $H_2S$ das Radon quantitativ vom Argon und Neon getrennt. Hier treten die Kristalle der betreffenden Stoffe gleichsam als ein Atomsieb auf, das in seinen Zellen die grösseren Radonatome aufhält, dagegen die kleineren Atome des Neons (oder des Heliums) durchlässt. Wenngleich die Atome des Argons ihrer Grösse nach diesen Zellen entsprechen, so werden sie doch nur in geringer Anzahl aufgehalten, da sie eine bedeutend geringere Bindungsenergie besitzen, als die Atome des Radons und die Moleküle der untersuchten Stoffe.

Die gewonnenen Ergebnisse zeigen, dass die schweren Edelgase mit den flüchtigen Hydriden—HCl, HBr und $H_2S$, die ein grosses Dipolmoment besitzen—Mischkristalle bilden. Ferner bilden sie Mischkristalle (vielleicht nur in engen Grenzen) mit Stoffen, deren Moleküle aus mehreren Atomen bestehen, wie $SO_2$. $CO_2$ und $CH_3COCH_3$. Da in den Molekulargittern der isomorphe Ersatz durch ganze Moleküle geschieht, so hängt hier die Bildung der Mischkristalle offenbar nicht von der Anzahl der Atome im Molekül ab, sondern hauptsächlich von der Grösse der einander ersetzenden Teilchen.

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*CHEMIE*

# ÜBER DIE CHEMIE DER EDELGASE. V. VERBINDUNG DES RADONS MIT PHENOL

Von B. A. NIKITIN

*(Vorgelegt von V. G. Chlopin, Mitglied der Akademie, d. 21. VI. 1939)*

Bisher ist nur eine Gruppe chemischer Verbindungen der Edelgase einwandfrei festgestellt worden, das sind die Kristallhydrate mit 6 Molekülen Wasser. Aus diesem Beispiel ist zu ersehen, dass die Edelgase, Molekülverbindungen, die durch die van der Waalsschen Kräfte bedingt sind, zu bilden vermögen. Den vorliegenden Untersuchungen liegt der Gedanke zugrunde, dass die Edelgase hinsichtlich ihres Vermögens Molekülverbindungen zu geben, zahlreiche Analoga unter den anderen Stoffen besitzen. Dieses sind vor allem die flüchtigen Hydride, deren Moleküle sich wie Pseudoatome verhalten. Analog den Edelgasen verhalten sich ferner Stoffe mit typischer Atombindung deren Moleküle, obwohl sie aus mehreren Atomen aufgebaut sind, in erster Näherung als Sphären mit den Dimensionen von derselben Grössenordnung wie die der Atome von schweren Edelgasen betrachtet werden können ($SO_2$, $C_2H_6$ u. a.). Die Stabilität der Molekülverbindungen hängt von der Teilchengrösse und der Grösse der van der Waalsschen Kräfte ab. Unaufgeklärt bleiben bisher die Bedingungen, die die Bildung der Molekülverbindungen verursachen. Es kann bisher nicht erklärt werden, weshalb diese Verbindungen in einigen Fällen entstehen, in anderen aber nicht gebildet werden können.

In Tabelle 1 sind vergleichsweise zwei Beispiele der Analogie der Teilchengrösse und der van der Waalsschen Kräfte in Anlehnung an die Theorie von London(1) bei Edelgasen und einigen flüchtigen Hydriden angeführt. In der Tat besitzen Methan und Krypton einerseits, Radon, Schwefelwasserstoff und Bromwasserstoff andererseits, nahe Siede- und Schmelztemperaturen.

Es sei hier noch erwähnt, dass die Analogie zwischen diesen Stoffen so weit geht, dass sie im Kristallgitter einander isomorph ersetzen können (2).

Tabelle 1

| | Radien $r$, $10^{-8}$cm | Polarisierbarkeit $\alpha$, $10^{-25}$ | Ionisationspotential $I$ | Dipolmoment $\mu$, $10^{-18}$ | Siedepunkt | Schmelzpunkt |
|---|---|---|---|---|---|---|
| Kr | 1.98 | 24.6 | 13.9 | — | 121° | 117° |
| $CH_4$ | 2.08 | 26.1 | 13.7 | — | 112° | 90° |
| Rn | ~2.2 | 54.2 | 10.7 | 0 | 210° | 202° |
| $H_2S$ | 2.05 | 37.8 | 10.4 | 0.93 | 213° | 190° |
| HBr | 2.04 | 35.8 | 13.2 | 0.78 | 206° | 187° |

Die Entdeckung der inerten Natur der Elemente der O-Gruppe, ihre Unfähigkeit, Salze oder Oxyde zu bilden, hat seinerzeit als Ausgangspunkt zur Aufstellung der Theorie der Ionenbindung gedient. Die Erforschung der Molekülverbindungen der Edelgase wird, unserer Meinung nach, für die Erkenntnis der Natur der gesamten Molekülverbindungen und der Gesetzmässigkeiten ihrer Bildung eine bedeutende Rolle spielen. Den ersten Schritt in diesem Sinne bedeutet die Feststellung der Analogie zwischen Edelgasen und anderen Stoffen. Methan und Krypton sind ihrer Teilchengrösse sowie der

Grössenordnung der van der Waalsschen Kräften nach so ähnlich, dass sie in allen Fällen gleiche Molekülverbindungen mit nahe zu derselben Beständigkeit bilden müssen. Radon unterscheidet sich von $H_2S$ und HBr dadurch, dass es kein permanentes Dipolmoment besitzt. Bei Molekülverbindungen, die hauptsächlich durch das Vorhandensein des Dipolmoments verursacht werden (z. B. $CS_2 . 6H_2S$), wird Radon kaum eine Analogie mit Schwefelwasserstoff aufweisen. Mit HBr wird Radon auch in denjenigen Verbindungen keine Analogie aufweisen, in denen die Moleküle von HBr dissoziiert sind, d. h. in den Oxonium- und ähnlichen Verbindungen. In Fällen hingegen, wo die Molekülverbindungen hauptsächlich durch die Polarisierbarkeit der Teilchen bedingt werden, muss sich Radon wie $H_2S$ und HBr verhalten. Diese Vorstellungen eröffnen grosse Möglichkeiten, neue Gruppen von chemischen Verbindungen der Edelgase darzustellen. Leider ist die Chemie der Molekülverbindungen noch sehr wenig erforscht. Es sind bisher nur wenige Verbindungen für die Analoga der Edelgase bekannt. Als solche kann die Verbindung von Schwefelwasserstoff mit Phenol $H_2S . 2C_6H_5OH$ genannt werden, die von Terres und Vollmer[3]) an Hand der Erstarrungskurven entdeckt wurde. Sie schmelzt kongruent bei +47.4°C. Von den anderen Molekülverbindungen des Phenols ist nur $H_2O . 2C_6H_5OH$ bekannt, die fälschlich als Phenolhydrat bezeichnet wird. Ist für die Bildung derartiger Verbindungen mit Phenol das Vorhandensein eines Dipolmomentes nicht durchaus notwendig, so müssen derartige Verbindungen auch mit Edelgasen existieren. Derartige Verbindungen müssen ebenso zahlreich auftreten, wie die Kristallhydrate.

Terres und Vollmer erhielten die Verbindung von Schwefelwasserstoff mit Phenol durch Abkühlung der flüssigen Gemische beider Komponenten. Für unsere Zwecke war dieses Verfahren unzweckmässig, weshalb wir ein anderes Verfahren anwandten. Bei der Einwirkung des Gases auf zerkleinertes festes Phenol bei Zimmertemperatur bildet sich diese Verbindung nicht. Es ist notwendig das Reaktionsgefäss auf —35°C abzukühlen, dann beginnt der Druck im Gefässe schnell zu sinken. Bei Anwesenheit von Kristallkeimen der Verbindung verläuft die Reaktion bei Zimmertemperatur verhältnismässig schnell. Die Verbindung von Schwefelwasserstoff mit Phenol dissoziiert in ihre Bestandteile, wobei jeder Temperatur ein bestimmter Dissoziationsdruck entspricht:

| $t$ | —10°C | 0° | +15° | +20° | +25.3° |
|---|---|---|---|---|---|
| $P$ mm | 108 | 198 | 440 | 580 | 760 |

Der Logarithmus $P$ ist eine lineare Funktion der Temperatur. Wie wir sehen, erweist sich die Verbindung $H_2S . 2C_6H_5OH$ bedeutend stabiler als das $H_2S$-Hydrat, dessen Dissoziationsdruck bereits bei +0.3°C 1 Atm. erreicht.

In den vorangehenden Mitteilungen wurde eine neue Darstellungsmethode für dissoziierende Verbindungen beschrieben[4]). Diese Methode beruht auf der Mitausscheidung des zu untersuchenden Gases bei der Bildung einer analogen isomorphen Verbindung eines anderen Stoffes. Bildet Radon (b. z. w. Argon) eine analoge Verbindung mit Phenol, so muss Radon bei der Bildung von $H_2S . 2C_6H_5OH$ aus gasförmigem $H_2S$ und Phenol in Gegenwart von Radon ebenfalls ausfallen. Insofern Rn und $H_2S$ tatsächlich Mischkristalle zu bilden vermögen, so müssen auch sämtliche analog gebauten Molekülverbindungen isomorph sein. Wie Chlopin und seine Mitarbeiter[5]) gezeigt haben, kann die Anwendbarkeit des Berthelot-Nernst'schen Gesetzes auf die Verteilung der Mikrokomponente zwischen der festen kristallinischen und der flüssigen (in unserem Falle der gasförmigen) Phase als Beweis der isomorphen Mitausscheidung dienen. Die Verteilungskonstante

$$D = \frac{\% \text{ Rn in Krist.} \times \% \ H_2S \text{ in Gas}}{\% \text{ Rn in Gas} \times \% \ H_2S \text{ in Krist.}}$$

muss unveränderlich bleiben, unabhängig von relativem Mengenverhältnis der beiden Phasen. Die feste Lösung muss verdünnt sein, d. h. die Kristalle müssen nur eine geringe isomorphe Beimischung der Edelgase enthalten und mehrfach umkristallisiert werden damit die Verteilung des Radons zwischen der festen und der gasförmigen Phase den Gleichgewichtszustand erreicht.

Die Versuche wurden bei +15°C ausgeführt. Das Eutektikum Phenol—$H_2S \cdot 2C_6H_5OH$ liegt bei +36°C[2], deshalb bestand das System aus zwei festen Phasen (Phenol und die Verbindung) und einer Gasphase. Wie die Blindversuche zeigten, wurde das Radon von dem Phenol selbst nicht aufgenommen. Der Gleichgewichtszustand kann nach drei Wegen erzielt werden. Man kann die Verbindung $H_2S \cdot 2C_6H_5OH$ in einem U-förmigen Rohr erhalten, sodann gibt man Radon (1 ml Luft, c. $10^{-12}$ g Rn enthaltend) dazu und kristallisiert die $H_2S$-Verbindung mehrfach um, wobei das Radon in die Kristalle übergeht (Weg von «unten»). Oder man kann fast 100% $H_2S$ und Rn bei niedriger Temperatur ausscheiden und bei +15°C umkristallisieren (Weg von «oben»). Endlich, kann man die Ausscheidung der $H_2S$-Verbindung in Gegenwart von Rn durchführen, da frühere Untersuchungen mit den Hydraten bewiesen haben, dass während der Bildung der Kristalle ihre mehrfache Umkristallisation stattfindet. Nach Abschluss des Versuches wurde das Radon sowohl in der Gasphase wie auch in Kristallen bestimmt (Tabelle 2).

Tabelle 2

| Methode | Zeitdauer | Ausgesch. $H_2S$ in % | Ausgesch. Rn in % | $D$ |
|---|---|---|---|---|
| Kontrolle | 2 Tage | 0 | 0.15 | — |
| Weg von unten | 15 Min. | 40 | 3.0 | — |
| » » » | 2 Tage 22 St. | 49.0 | 53.5 | 1.19 |
| Ausscheidung | 15 Min. | 51.1 | 57.2 | 1.28 |
| » | 15 Min. | 59.5 | 65.7 | 1.30 |
| Weg von unten | 4 Tage 22 St. | 73.1 | 77.3 | 1.25 |
| Ausscheidung | 15 Min. | 75.4 | 80.0 | 1.30 |
| Weg von oben | 3 Tage 20 St. | 87.1 | 89.0 | 1.20 |

Man sieht, dass das Radon mit den Kristallen $H_2S \cdot 2C_6H_5OH$ mitausgefällt wird, wobei die Verteilungskonstante $D$ innerhalb der Versuchsfehler tatsächlich konstant bleibt. Folglich bildet Radon eine analoge Molekülverbindung $Rn \cdot 2C_6H_5OH$, die bedeutend stabiler ist als deren Hydrat[4], da sie sehr leicht bei Zimmertemperatur erhalten wird. Inre Stabilität ist, wie wir auch vermuteten, ungefähr gleich der Stabilität der $H_2S$-Verbindung, da der Wert der Konstante $D$ etwa 1 beträgt. Demzufolge muss auch ihre Schmelztemperatur von der Grössenordnung +50°C sein. Es ist bemerkenswert, dass die Verbindungen mit Phenol, im Gegensatz zu den Hydraten, kongruent schmelzen. Es ist möglich, dass sie auch in flüssigem Zustand existieren können. Wir sehen, dass ein Dipolmoment für die Bildung einer Verbindung mit Phenol nicht unbedingt notwendig ist. Argon scheidet sich ebenfalls mit $H_2S \cdot 2C_6H_5OH$ aus, wobei die Verteilungskonstante $D$ 0.002 beträgt. Analoge Verbindungen wurden von uns auch für $SO_2$, HCl und HBr erhalten, wobei die Geraden log $P$—$t$ für alle diese Verbindungen parallel verlaufen.

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*CHEMIE*

# VIRTUELLE ENTROPIE DES SILICIUMFLUORIDS, BERECHNET AUS DEN MOLEKULARKONSTANTEN

Von I. G. RYSS

*(Vorgelegt von A. N. Terenin, Mitglied der Akademie, d. 16. VI. 1939)*

Die von Brokway u. Wall(1) und H. Braune u. Pinnow durchgeführten Untersuchungen der .Elektronenbeugung im gasförmigen Siliciumfluorid haben gezeigt, dass $SiF_4$ eine tetraedrische Struktur hat, mit dem Atomabstand Si—F $r=1.54$ Å(1) oder 1.55 Å (2).

Wenn wir den Atomabstand Si—F als $r=1.55$ Å, das Atomgewicht des Fluors als 19.00 und die Avogadrosche Zahl $N$ als $6.06\cdot10^{23}$ annehmen, so wird das Trägheitsmoment der $SiF_4$-Molekül

$$J_1=J_2=J_3=\frac{8}{3}\frac{A}{N}r^2=200.9\cdot10^{-40}\ \text{g/cm}^2$$

betragen.

Die Grundschwingungen des $SiF_4$ sind aus den Ramanspektren [Yost u. Mitarbeiter (3)] und aus den infraroten Spektren [Bailey u. Mitarbeiter(4)] ermittelt. Sie sind in Tabelle 1 angeführt.

Tabelle 1

| Schwingung | Entartungsgrad | Wellenzahl in $cm^{-1}$ | Autor und Methode |
|---|---|---|---|
| $\nu_1$ | 1 | 800 | Yost. Ramanspektrum. |
| $\nu_3$ | 3 | 1022 | Bailey. Infrarot Spektrum. Band der maximalen Intensivität |
| $\nu_4$ | 3 | (420) | Bailey. Berechnet aus Kombinationstönen des infraroten Spektrums |
| $\nu_2$ | 2 | (260) | |

Die Schwingungen $\nu_2$ und $\nu_4$, welche den grössten Einfluss auf die Grösse der Vibrationsentropie des $SiF_4$ haben, sind in dem Ramanspektrum (3) inaktiv und befanden sich ausser dem Gebiet der Ausmessung des infraroten Spektrums. Man kann doch annehmen, dass die in der Tab. 1 angegebenen Schwingungsfrequenzen ziemlich genau sind: die grösste Abweichung des Zentrums des infraroten Streifens von der berechneten Grösse kommt—25 $cm^{-1}$gleich (für $\nu_2+\nu_4$). Weniger zuverlässig, aber doch den in der Tabelle 1 angegebenen Schwingungsfrequenzen nahekommend, sind die von Yost aus den Verhältnissen zwischen den Grundschwingungen anderer Tetrahalogenide berechneten Grössen: $\nu_2=285$, $\nu_3=1000$ und $\nu_4=431$ $cm^{-1}$, sowie auch die von Bailey auf analoge Weise berechneten Werte für $\nu_2=304$ und $\nu_4=447$ $cm^{-1}$.

Die Berechnung der virtuellen Entropie des $SiF_4$ (Tabelle 2) wurde nach der bekannten Näherungsformel ausgeführt:

$$S = 4.573 \left\{ 4\log T + \frac{3}{2}\log M + \frac{1}{2}\log J_1 J_2 J_3 + \log s + \log g_0 + \right.$$
$$\left. + \sum \left[ \frac{\Theta}{T} \frac{0.4343}{\exp\left(\frac{\Theta}{T}\right) - 1} - \log\left[ 1 - \exp\left( -\frac{\Theta}{T} \right) \right] \right] \right\} + 265.349$$

Das Quantengewicht $g_0$ wird als 1 angenommen, was für andere tetraedrische Molekülen zutrifft; die Symmetriezahl $s=12$; das Molgewicht $M = 28.06+4\cdot19.00=104.06$; $T$ ist vorstehend berechnet worden; die Grundschwingungsfrequenzen sind in Tabelle 2 angeführt.

Tabelle 2

Virtuelle Entropie des $SiF_4$ von 298.2 bis 573.2° abs.

| Temperatur | | Entropie in cal/°C mol. | | |
|---|---|---|---|---|
| °C | °abs. | Transl. + rotat. | Vibrat. | Summe |
| 25.0 | 298.2 | 60.932 | 6.507 | 67.439 |
| 100.0 | 373.2 | 62.714 | 8.846 | 71.560 |
| 126.8 | 400.0 | 63.226 | 9.650 | 72.876 |
| 200.0 | 473.2 | 64.600 | 11.747 | 76.347 |
| 226.8 | 500.0 | 64.999 | 12.477 | 77.476 |
| 300.0 | 573.2 | 66.123 | 14.371 | 80.494 |

Die Genauigkeit der Berechnung ist hauptsächlich von den Fehlern für die Werte $\nu_2$ und $\nu_4$ beeinflusst. Wenn wir z. B. $\nu_2=285$ $cm^{-1}$ annehmen, so müssen die in der Tabelle 2 angegebenen Grössen um 0.317 cal/° C mol. bei 298.2° abs. und um 0.351 cal/° C mol. bei 573.2° abs. verkleinert werden. Weniger einflussreich ist der mögliche Fehler bei der Atomabstandbestimmung. Wenn man z. B. $r=1.54$ Å (nach Brokway) annimmt, so wird $J=198.3\times 10^{-40}$ $g/cm^2$, und dann müssen die oben berechneten Entropiegrössen um eine geringe und temperaturkonstante Grösse (0.039 cal/° C mol.) verkleinert werden.

Man kann annehmen, dass die berechneten Entropiegrössen nicht mehr als um 0.5 cal/°C mol. von den wirklichen Grössen abweichen. Ein derartiger oder sogar doppelt so grosser Fehler spielt bei Gleichgewichtsberechnungen eine kleinere Rolle, als der mögliche Fehler, der bei der Bestimmung der Bildungswärme des Siliciumfluorids entsteht.

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*GEOCHEMIE*

# DIFFUSIONSWÄRME DES HELIUMS ALS KRITERIUM FÜR DIE BRAUCHBARKEIT VON MINERALIEN FÜR ALTERSBESTIMMUNGEN NACH DER HELIUMMETHODE

Von E. K. GERLING

*(Vorgelegt von V. G. Chlopin, Mitglied der Akademie, d. 15. VI. 1939)*

Auf dem internationalen Geologen-Kongress 1937 in Moskau(1) habe ich die Diffusionswärme des Heliums als Kriterium, welches die Brauchbarkeit von Mineralien für Altersbestimmungen nach der Heliummethode anzeigt, vorgeschlagen. Die Diffusionswärme kennzeichnet den energetischen Zustand des Heliums, sowie der Atome des festen Stoffes, bei welchem der Übergang des Heliums von einer Elementarzelle zur anderen stattfindet. Es konnte gezeigt werden, dass mit dem Ansteigen der Grösse der Diffusionswärme die Wahrscheinlichkeit der Verschiebung des Heliums innerhalb des Kristallgitters sinkt. Die Diffusionswärme kann einerseits berechnet, andererseits experimentell ermittelt werden. Die Diffusionswärme lässt sich auf Grund der Theorie von Jean Cichocki(2) berechnen, allerdings nur für Metalle.

Die von mir ausgeführte Berechnung ergab, dass alle Metalle mit einem Schmelzpunkt über 1000°C einen hohen Wert für die Diffusionswärme ergeben und somit die Wahrscheinlichkeit von Helium-Verlusten innerhalb $2\times10^9$ Jahren praktisch gleich Null ist. Der Grenzwert der Diffusionswärme, welcher noch die Erhaltung des Heliums in Mineralien innerhalb der Zeit von $2\times10^9$ Jahren verbürgt, gleicht, wie die Berechnung ergibt, ungefähr 35—36000 cal. pro Grammatom Helium; daher müssen Mineralien, die einen derartigen oder grösseren Wert der Diffusionswärmen besitzen, brauchbar für Altersbestimmungen nach der Heliummethode sein.

Wie erwähnt, gibt es einen zweiten Weg für die Bestimmung der Diffusionswärme, die auf der Theorie von G. L. Grünberg(3) der Entgasung von Metallen im Vakuum beruht. Dieser Forsher stellte folgende Formel für die pro Zeiteinheit abgegebene Gasmenge beim Erwärmen eines zylindrischen Fadens auf:

$$\frac{dQ}{dt} = 2\pi DNe^{\frac{-5.78D}{R^2}};$$

hierin bedeuten: $D$—den Diffusionskoeffizienten; $N$—Anzahl der Gasatome; $R$—Radius des Fadens; $t$—die Zeit. Diese Gleichung wurde von Ptizin und Fink(4) experimentell geprüft, wobei, wie auch zu erwarten war, gefunden wurde, dass $\lg\frac{dQ}{dt}$ sich geradlinig mit der Zeit ändert. Ausserdem stellten diese

Autoren die Abhängigkeit zwischen der Temperatur und dem Diffusionskoeffizienten fest: $D = D_0 e^{\frac{-E}{RT}}$. Nach Auftragen der $\lg D$-Werte längs der Ordinate und der $\frac{1 \cdot 10^6}{T}$-Werte längs der Abszisse, erhielten sie eine Gerade, auf Grund welcher die Werte für die Diffusionswärme berechnet wurden. Ich versuchte nach dieser Methode die Diffusionswärme des Heliums für einige Mineralien zu bestimmen und die Abhängigkeit zwischen dem erhaltenen Werte für die Diffusionswärme und der von den Mineralien abgegebenen Heliummenge festzustellen. Untersucht wurden die in der Tabelle angeführten Mineralien.

| Mineral | Alter nach der He-Methode in $10^6$ Jahre | % des He-Verlustes | Diffusionswärme in cal. pro Grammatom Helium | | | |
|---|---|---|---|---|---|---|
| | | | I | II | III | IV |
| Massive Loparit-Stücke, 1—2 mm . . . . . | 280 | <10 | — | 34 300 | — | — |
| Poykilitische Loparit-Stücke, 1—2 mm . . | 170 | 40 | 22 300 | 34 000 | — | — |
| Monazit-Körner, 0.2—0.5 mm . . . . . | 852 | 47 | 6 300 | 27 800 | 41 400 | 50 300 |
| Monazit-Staub, <0.1 mm | 852 | 47 | — | 28 700 | 40 500 | — |
| Uraninit-Körner, 0.2—0.5 mm . . . . . | 48 | 97 | 9 600 | 15 000 | — | — |

Für die Bestimmung der Diffusionswärme wurde ein spezieller Apparat konstruiert, dessen Beschreibung an anderer Stelle gegeben wird; es sei jedoch darauf hingewiesen, dass dieser die Möglichkeit, die pro Minute abgegebene Heliummenge, sowie den zeitlichen Verlauf der Heliumabgabe durch

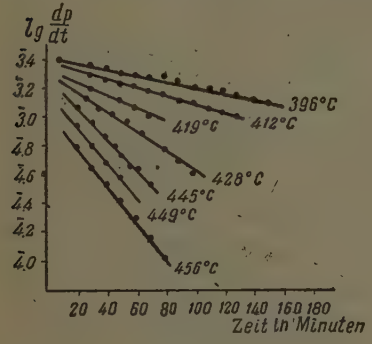


Fig. 1.

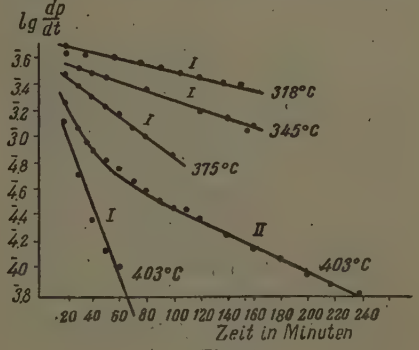


Fig. 2.

das Mineral, zu verfolgen, gestattet. Der Logarithmus der durch die Einwage des Minerals pro Minute abgegebenen Heliummenge wurde längs der Ordinate, die Zeit längs der Abszisse aufgetragen, hierbei wurden Kurven erhalten, welche den Prozess der Heliumabgabe durch das Mineral für verschiedene Versuchstemperaturen kennzeichnen.

Die Ergebnisse dieser Bestimmungen für massive, sowie poykilitische Loparite sind in den Diagrammen 1—3 angeführt. Für massiven Loparit wurden, wis aus den Diagrammen ersichtlich ist, Gerade erhalten, deren Neigungswinkel mit der Temperatur ansteigt. Trägt man längs der Ordinaten den

Logarithmus des Neigungswinkels, der für vershiedene Temperaturen erhalten wurde, längs der Abszisse den Wert $\frac{1}{T} \cdot 10^6$ auf, so erhält man eine Gerade, auf Grund welcher der Wert für die Diffusionswärme berechnet wurde. Für massiven Loparit betrug diese 34 300 cal. pro Grammatom Helium (Diagramm 4). Für poykilitischen Loparit wurde ein anderer Verlauf der Heliumabgabe festgestellt, was aus den Diagrammen 2 und 3 zu ersehen ist. Für die Temperaturen 318, 345 und 375°C wurden Gerade erhalten, deren Neigungswinkel mit der Temperatur ansteigt. Bei 403° wurde statt einer Geraden eine Kurve erhalten, die aus zwei geradlinigen Teilen besteht. Es wird vermutet, dass der mittlere Teil dieser Kurve infolge Überlagerung zweier Prozesse, die ihren Ursprung in der Heliumabgabe aus zwei vershiedenen Zuständen des

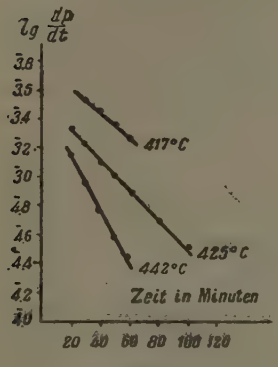

Fig. 3.

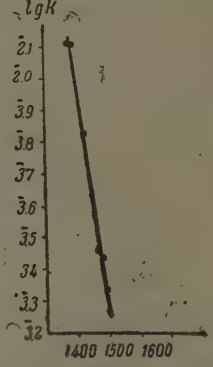

Fig. 4.

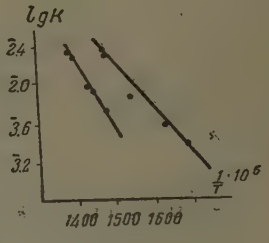

Fig. 5.

Minerals haben, ensteht. Wenn man annimmt, dass jeder dieser Prozesse unabhängig verläuft, so kann man eine Korrektur einführen, die den Einfluss des zweiten Prozesses auf die durch den ersten Prozess abgeschiedene Heliummenge berücksichtigt. Die Ergebnisse dieser Berechnungen sind im Diagramm 2 wiedergegeben. Diesem Diagramm kann man entnehmen, dass die erhaltenen Punkte auf einer Geraden liegen. Bei weiterer Temperatursteigerung wurden wieder Gerade erhalten, da es nicht gelungen ist, diejenigen Abschnitte der Kurve festzuhalten, die die Heliumabgabe aus dem ersten Zustand kennzeichnen. Aus den erhaltenen Neigungswinkeln wurde die Diffusionswärme für jeden diesen Prozess berechnet, wobei diese für den ersten Prozess 22 300 cal. pro Grammatom Helium gleichkam und für den zweiten Prozess den Wert von 34 000 cal. ergab (Diagramm 5). Berücksichtigt man, dass poykilitische Loparite, worauf L. W. Komlew[5] hinwies, eine grosse Zahl von fremdartigen Einschlüssen enthalten, so muss man die Diffusionswärme von 22 300 cal. der Verschiebung des Heliums innerhalb des Kristallgitters des Loparits zuschreiben. Der erhaltene Wert von 34 000 cal. für die Diffusionswärme stimmt, wie ersichtlich, gut überein mit demjenigen Wert, der für massiven Loparit erhalten wurde. Dieselben Versuche wurden mit Monazit wiederholt, wobei für dieses Mineral eine ganze Reihe von Zuständen des Heliums festgestellt wurde. Die Abgabe des Heliums in diesen verschiedenen Zuständen hängt mit einer verschiedenen Aktivierung der Heliumatome und der Ionen des festen Stoffes zusammen. So beträgt z.B. die Diffusionswärme des Heliums, welches aus dem ersten Zustand abgegeben wird, im Ganzen 6300 cal. pro Grammatom Helium und ist anscheinend durch die Verschiebung des Heliums längs Spalten von 2—4 Å Breite bedingt. Die aus diesem Zustand

abgechiedene Heliummenge ist unbedeutend und beträgt im Ganzen 1—2% der gesamten im Mineral enthaltenen Heliummenge.

Für den zweiten Prozess ist die Diffusionswärme des Heliums gleich 27 800 cal. pro Grammatom Helium und ist wahrscheinlich durch die Diffusion des Heliums längs der Spaltflächen hervorgerufen, da eine Verschiebung des Heliums in dieser Richtung anscheinend dem geringsten Widerstand begegnet. Zwei weitere Diffusionswärmen betrugen 41 400 bzw. 50 300 cal. pro Grammatom und werden durch Heliumabgabe aus verschiedenen Teilen des Monazitgitters bedingt.

Für Uraninit wurden zwei Diffusionswärmen erhalten, die eine betrug 9600 cal. und ist wahrsheinlich, wie auch im Falle des Monazits, durch Ausscheidung des Heliums aus Rissen hervorgerufen; der zweite Wert beträgt 15 000 cal. und ist wohl durch Verschiebung des Heliums im Uraninitgitter bedingt.

Aus den erhaltenen Resultaten ist zu ersehen, dass die durch das Mineral abgegebene Heliummenge mit der Diffusionswärme des Heliums in dem Kristallgitter abnimmt und bei der Erreichung eines Wertes von 34 000 cal. pro Grammatom Helium, was z. B. bei Loparit der Fall ist, noch nicht einmal 10% beträgt. Auf Grund der experimentell ermittelten Diffusionswärmen ist der Schluss berechtigt, dass man auf Grund des Wertes für die Diffusionswärme über die Brauchbarkeit des betreffenden Minerals für Altersbestimmungen nach der Helliummethode schliessen kann, und dass ein Wert von 34 000 cal. die völlige Erhaltung der ursprünglichen Heliummenge verbürgt, vorausgesetzt, dass das Gitter dieser Mineralien frei von bedeutenden Störungen ist.

Ein ausführlicher Bericht über diese Arbeit erscheint in den «Arbeiten des Radium Instituts».

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Akademie d. Wissenschaften d. UdSSR.

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*AGROCHEMISTRY*

# REASONS FOR $P_2O_5$ PHOSPHORITE BEING MORE AVAILABLE TO PLANTS AFTER CHLORINATION

By V. V. BUTKEVICH, A. A. GERMANOV and K. I. GADALOVA

*(Communicated by D. N. Prianishnikov, Member of the Academy, 7. VI. 1939)*

Evidence produced at the laboratory of D. N. Prianishnikov has shown with sufficient clearness the harmful activity of calcium in the nutrient medium. When this compound is present there, the plants decrease in the ability of absorbing phosphorus out of various sparingly soluble phosphates of calcium, and it has been stated specially that harvest is strongly reduced by the introduction of calcium carbonate in the case of phosphorite, while in the case of soluble phosphate the introduction of calcium carbonate has no appreciable effect on harvest(1). That $CaCO_3$ tends to act unfavourably in this direction has also been reported by K.K. Gedroiz(2), O. K. Kedrov-Sikhman(3), V. F. Chirikov(4) and others.

If this was so with the $CaCO_3$ added experimentally to the nutrient medium by the above authors, it should not be otherwise indeed with the $CaCO_3$ contained in the phosphorite. There are even some grounds to suppose the latter to have added deleterious influence, while making the phosphorite less effective than the other phosphates. Its presence immediately in the zone of contact between the radicle and the phosphorite particle and its higher solubility compared to the phosphorite of the calcium phosphorite cannot but paralyze the dissolving action of the root system upon those phosphate compounds of the phosphorite. It is only after $CaCO_3$, and in the first instance its most active part, has broken down, that the carbon dioxide can considerably, as is shown hereafter, increase in ability to dissolve the phosphate compounds of the phosphorite. The same is true of iron phosphates and alumina which are also contained in the phosphorite and whose availability is also reduced, if not so strongly, by the presence of excessive $CaCO_3$ in the nutrient medium(1).

It is an established fact that acid soils not saturated with bases absorb calcium eagerly and create conditions for the phosphorite to become so effective as fertilizer that it sometimes ranks with superphosphate (9—12). If, however, the above characters are weakly expressed in the soil, the phosphorite meal must long (for several years) lie in it to approach the superphosphate in its action on the first planted culture(11).

Two questions arise here. What changes have to take place in the phosphorite particles in order that its action on plants may approach to that of a soluble phosphate? Is it necessary or not, with regard to the bulk of our soils responsive to phosphorus, to endeavour as strong a decomposition of the phosphorite meal as is reached, for instance, in the process of superphosphate production? The essentially important side to these questions is that their solution will permit the technology of phosphate fertilizers better to meet the varying requirements of the principal soil belts in this country. This approach to the problem will make it possible to increase the effectiveness of the reagents which, if used in the treatment of phosphorite meal, can in a number of cases restrain the retrogression of its $P_2O_5$ in the soil.

The technical process of superphosphate production as it is conducted today needs about 741 kg of sulphuric acid (calculated for monohydrate) per a ton of phosphorite meal, or 644 kg of monohydrate per a ton of apatite (concentrate).

The process of chlorination elaborated by us (without external heating) is based upon the ability of phosphorite meal particles freely to absorb chlorine gas, and it is about 50 kg of chlorine per ton of phosphorite which are thus absorbed. The changes which take thereby place in phosphorite particles do not lead to transition of the bulk of phosphoric acid into water soluble condition, and there is no danger therefore of its retrogression in the soil. On the other hand, these changes are strong enough to increase the availability of $P_2O_5$ phosphorite to plants considerably.

Our experiments with the phosphorites from Egorievsk have shown that an appreciable (about $^1/_3$) and the most active part of the $CaCO_3$ phosphorite is destroyed by chlorine. As a result of chlorination this hydrolytically alkaline salt is converted into $CaCl_2$. Accordingly, the carbon dioxide from the balloon (and also that evolved by roots) is no longer apt to call forth the formation of bicarbonate calcium in the solution, a substance whose harmful effect, as observed in a specially arranged physiological experiment([14]), is to restrain the ability of plants to absorb phosphorus out of $Ca_3(PO_4)_2$.

Chlorination of the phosphorite made its aqueous extract (1 : 5) change in pH from 6.5—7.0 to 3—3.5. The acidity of this extract, as determined by titration against phenolphtalein, became 100—240 $cm^3$ of 0.1 *n* Ba $(OH)_2$ per 100 g of chlorinated phosphorite. This increase in acidity of the phosphorite meal must be credited to have only a positive influence on the availability of $P_2O_5$ phosphorite to plants, inasmuch as with regard to peat, physiologically acid salts and soil the acidification is known to produce such influence. The chlorination of the phosphorite meal having a percentage of moisture equal to 1.5% increased its content of water soluble $P_2O_5$ from 0.01% (in the initial product) to 3.7% (of the total content of $P_2O_5$), whereby the moisture increased to 7.7—6.6% (1.13% of the weight of phosphorite meal). The amount of available $P_2O_5$ in the phosphorite meal (estimated according to Petermann) increased 10 times under the influence of chlorine, viz. from about 0.3% (by weight) to 2—3% (10—15% of total $P_2O_5$). Calculations show that 1 kg of available $P_2O_5$ is obtained by consumption of 1.7—2.5 kg chlorine (in the case of chlorinated phosphorus) or of 3.6—4.2 kg of sulphuric acid (in the case of superphosphate). These are very interesting figures indeed. Not only do the former compare favourably with the latter in respect of the effectiveness of the different reagents applied in treating the phosphorite meal, but the principal advantage is the possibility to enrich the fertilizers with phosphoric acid which is readily available to plants and whose production in this country is limited by the shortage of sulphuric acid. Thereby an important new item is established in the domain of economic utilization of chlorine. It should be mentioned here that our investigation was largely run with the phosphorites from Egorievsk which, as well as the other phosphorites in this country, are not suitable to superphosphate production. The latter is now based on the apatites which have to make a long way before they reach the Voskresensky chemical works (about 2000 km by rail from Kolsky peninsula).

Laboratory experiments have shown that the dissolving action of carbon dioxide upon phosphorite particles is increased after chlorination. It is an important statement from the viewpoint of our inquiry into the mechanism of the different action of plant roots upon the particles of phosphorite meal and the particles of chlorinated phosphorus. The increased dissolving effect of carbon dioxide upon chlorinated phosphorus is easy to explain by the des-

truction of the most active part of $CaCO_3$. This effect was observed in five consecutive water extracts, and no limit could be established in the difference between the activity of $CO_2$ in the case of chlorinated phosphorite and its activity in the case of phosphorite meal.

Table 1

| Succession of extracts on saturation of water by $CO_2$ (from balloon) | I | II | III | IV | V | Total extracted |
|---|---|---|---|---|---|---|
| Extracted $P_2O_5$ in g per 1 kg of fertilizer | | | | | | |
| From phosphorite meal . | 0.042 | 0.028 | 0.036 | 0.047 | 0.037 | 0.19 |
| From chlor. phosphorus | 1.45 | 1.42 | 1.50 | 1.43 | 1.40 | 7.20 |
| Extracted CaO in g per 1 kg of fertilizer | | | | | | |
| From phosphorite meal . | 2.18 | 1.63 | 1.02 | 0.77 | 0.66 | 6.26 |
| From chlor. phosphorus . | 30.72 | 15.14 | 8.03 | 2.27 | 2.01 | 58.17 |

The succession of extracts from phosphorite meal and chlorinated phosphorus made according to Petermann have shown the content of available $P_2O_5$ to be always higher in the latter than in the former, though this difference goes gradually down.

Table 2

Percentage of available $P_2O_5$ (according to Petermann) in dry matter

| Succession of extracts | I | II | III | IV | Total |
|---|---|---|---|---|---|
| From phosphorite meal . . . . . | 0.40 | 0.37 | 0.36 | 0.41 | 1.54 |
| From chlorinated phosphorus . . . | 2.61 | 0.62 | 0.48 | 0.52 | 4.23 |

A positive effect, too, was obtained with the treatment in question in vegetative experiments, when hydrogen chloride was used instead of chlorine. Another evidence furnished by these experiments is that the processes of exothermic chlorination of the phosphorite meal which proceed without external heating, but even with evolution of heat, make not only phosphorus more easily available to the plant, but other elements too as sulphur and «microelements», and this will be shown in a further publication.

It is well to point out in conclusion that no decrease in the physical qualities of the phosphorite meal was produced by the process studied and the meal preserved its very fine grade and was easy to scatter.

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*GENETICS*

# ANALYSIS OF LINKAGE IN SHEEP

By B. N. VASSIN

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The existence of groups of genes safely proved in laboratory animals and in many plant species has so far not been assuredly established in large domestic animals. The slow rate of their multiplication and, hence, meagre knowledge of the inheritance of characters along with great chromosome numbers account for the lack of information on linkage. Among animals of practical importance linkage has been established only in fowl and rabbits, i. e. in the most prolific animals.

Owing to the complexity and time-consuming character of the work on linkage in domestic animals, locating individual genes affecting economically valuable characters is of limited importance for practical breeding. It is the more so as the quantitative characters depend on a great number of hereditary and non-hereditary factors so that their genetical analysis cannot be restricted to the study of individual genes. However, the fact that linkage has been established in large farm animals is of interest, since it may contribute to disclosing in them the same regularities of inheritance of characters which are operative throughout both animal and vegetable kingdoms. Linkage studies may, besides, bring us nearer to the problem of inheritance of concrete quantitative characters, the most raw ideas existing so far on this subject.

We considered it necessary, therefore, to analyze data on interrelation between certain genes and characters in segregation obtained in the breeding work on sheep. It was found in the first work on this subject (1) that there is no connexion in segregation between genes for adventitious nipples, wattles and pie-baldness (*Pn*) in sheep. The second work on linkage in sheep was that by J. L. Glembotsky (2) who has pointed to the great probability of a very strong linkage between genes causing cryptorchy and presence of horns in Precoces.

In 1939 we obtained sufficient material on crosses in coloured Astrakhan sheep; it enabled us to conduct an analysis for linkage of some of the genes and characters. The ram No. 261 «sur» as to the colour of its hair and having a first class pick on the ear, had wattles and shortened ears. The first of these characters is caused by the gene *W* (sheep lacking wattles are *ww*) and the second by the gene *a* (sheep with ears of normal length are *AA*, those with shortened ears—*Aa*, and earless—*aa*). This ram was crossed with females which were in the great majority of cases *AAww* (ears of normal length, no wattles).

There were obtained 430 lambs which were distributed in the following way: *AAW*—87 or 20%, *AaW*—101 or 24%, *AAww*—104 or 24%, *Aaww*—138 or 32%, where the ratio *W*: *ww*—0.44 : 0.56 and the ratio *AA* : *Aa* = =0.45 : 0.55. The deviation of these ratios from 0.50 : 0.50 (or 1 : 1) should

be explained by the presence of *Aa*-animals among the females and by the fact that a small fraction of wattles could be overlooked, especially in those cases when they were too small.

In the case of such a ratio of the two groups the relations between the four genotypes should be the following ones in absence of linkage:

| | *W*—44% | *ww*—56% |
|---|---|---|
| *AA*—45% | *AAW*—20% | *AAww*—25% |
| *Aa*—55% | *AaW*—24% | *Aaww*—31% |

which very closely agrees with the figures found in experiment. The two genes, consequently, are inherited independently of each other, hence they are located either in dfferent chromosomes or at a great distance within a common chromosome, so that in 50% of cases crossing-over can occur.

Connexion between these two genes and the various Astrakhan sheepskin qualities was further traced. The 430 lambs from the ram No. 261 were accordingly divided into the two following groups: 1) possessing wattles, 2) lacking them. The two groups were compared with each other in respect to size, shape and looseness of the curl and class of Astrakhan sheepskin. The same lambs were divided into the following two groups: 1) possessing normal ears (*AA*) and 2) possessing shortened ears (*Aa*). The individuals of these groups were again compared with one another as above. The results are presented in Table 1 (in %).

Table 1

| Group characters | *n* | Size of the curl | | | Pattern of the curl | | | | | Looseness of the curl | Class of Astrakhan sheepskin | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | large | medium | small | roll | bean-roll | bean-like | mixed | negative | | I | II | III |
| *W* | 184 | 67.4 | 31.5 | 1.1 | 6.5 | 39.1 | 48.9 | 4.9 | 5.6 | 43.5 | 10.3 | 66.9 | 22.8 |
| *ww* | 246 | 68.3 | 29.7 | 2.0 | 6.9 | 39.8 | 45.1 | 7.3 | 0.9 | 37.7 | 10.6 | 64.0 | 24.4 |
| *AA* | 180 | 69.4 | 28.9 | 1.7 | 6.7 | 40.0 | 50.0 | 3.3 | 0.0 | 41.7 | 9.4 | 66.1 | 24.5 |
| *Aa* | 226 | 67.3 | 31.4 | 1.3 | 5.8 | 38.0 | 46.5 | 8.4 | 1.3 | 33.6 | 9.7 | 65.1 | 25.2 |

It may be seen from Table 1 that there are no perceptible difference in Astrakhan sheepskin qualities either among the lambs of the first two groups or among those of the last two groups. The relation of the *W* and *A* genes to the duration of the embryonic development (E. D.) and to the weight at birth (W. B.) was considered; corresponding data are contained in Table 2.

Table 2

| Group characters | Male lambs | | | Female lambs | | |
|---|---|---|---|---|---|---|
| | *n* | E. D. | W. B. | *n* | E. D. | W. B. |
| *W* | 55 | 150.73±22 days | 5.27±0.8 kg | 58 | 150.28±20 days | 4.88±0.6 kg |
| *ww* | 72 | 151.13±21 » | 5.17±0.6 » | 61 | 150.80±20 » | 4.76±0.6 » |
| *AA* | 55 | 150.55±19 » | 5.16±0.7 » | 60 | 150.50±22 » | 4.81±0.6 » |
| *Aa* | 72 | 151.22±22 » | 5.25±0.6 » | 59 | 150.59±19 » | 4.83±0.7 » |

Table 2 shows that there was but a slight correlation between the characters studied and the genes *A* and *W*. Lambs *ww* are characterized by a longer period of embryonic development and at the same time possess smaller weight at birth than those of the *W* type (in males $+0.40 \pm 0.30$ days and $-0.10 \pm 0.10$ kg; in females $+0.52 \pm 0.28$ days and $-0.14 \pm 0.09$ kg). Although the difference between the groups was not great, the fact that it was of the same sign in ♂♂ and ♀♀ makes it highly significant. Besides, it was found previously that there is a positive correlation of the order $r=0.25-0.35$ between the duration of embryonic development and the weight at birth (for the progeny ♂ No 261 in all the ♂♂ $r=+0.29 \pm 0.08$); it was observed here that lambs of greater weight of the *W* groups have shorter period of embryonic development than those of the *ww* group, this being the case both among ♂♂ and ♀♀. Within each group positive conclusion is again observed (in ♂♂ of the *W* groups it equals +0.31, and in those of the *ww* group it equals +0.33). It may be stated on the basis of such an analysis that the gene *W* (or the genes which are localized in its vicinity) causes shortening of the period of embryonic development and increase in weight at birth.

A somewhat different relation between these characters was observed with respect to the *A* gene. Male lambs *Aa* have a longer period of embryonic development than those of the constitution *AA* ($+0.67 \pm 0.29$ days); in female lambs no such strong difference could be observed ($+0.09 \pm 0.29$ days). Both in ♂♂ and ♀♀ the *Aa* lambs are somewhat heavier than those of the constitution *AA*, i. e. a usual correlation between the two characters is observed. It may be supposed, therefore, that the *a* gene (or the genes localized in its vicinity) somewhat protract the embryonic development, thus increasing the weight at birth.

In the analysis of the progeny of ♂ No. 261 the mode of inheritance of the wattles was made clear. This character was described up to the present time as a simple dominant [3]. However, this proved not to be the case. Among 430 lambs obtained in 1939 from ♂ No 261 7 were found to possess on the necks instead of wattles two orifices surrounded by a wall-like outgrowth of the skin. A thick yellowish liquid was oozing out of these orifices; it reminded of blood-plasma. In all mothers of these lambs the wattles were found, so that it could be maintained that these lambs were homozygous for the *W* gene. Although mothers not of all the lambs have been examined for this character, it is known that in different herds of Astrakhan-sheep the percentage of animals with wattles varies from 10 to 18. The production of 7 homozygous lambs (*WW*) from a heterozygous ram (*Ww*) points to the fact that about 56 or 13% heterozygous females should have been present in the given herd, which closely corresponds to the average proportion of animals with wattles.

We had often to use in our work rams possessing wattles, however such rams never were homozygous, but gave a 1 : 1 segregation. On the basis of the above data as well as taking into consideration that homozygous lambs (*WW*) should be of low viability (easy penetration of infection through the orifices on the neck), it becomes greatly probable that sheep homozygous for wattles do not attain maturity and die at an early age like those homozygous for grey colour.

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*GENETICS*

# STUDIES ON THE NATURAL PROCESS OF MUTATION. II. RATE OF SPONTANEOUS MUTATION-PROCESS IN *DROSOPHILA MELANOGASTER*

By N. I. SHAPIRO

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The present paper is devoted to the discussion of data on the rate of spontaneous mutation in different chromosomes. The frequency of lethal mutations has been studied for the *X*, II and III chromosomes. The fourth chromosome has not been studied because of its small size. Asides from recording lethal mutations, the frequency of spontaneous occurrence of mutations causing sterility was studied. The frequency of occurrence of male steriles was studied for the *X*-chromosome; that of female steriles—for the II and III chromosomes. The experiment has been carried out under uniform external conditions, on a single laboratory stock. It should be emphasized that the method of detection of autosomal mutations used by us prevents confusion of cases of newly arisen mutations with cases of initial contamination. This holds true both for lethal and sterile mutations ([1],[2]).

The method used enabled us: 1) to compare the rate of spontaneous mutation in individual chromosomes and 2) to compare the rate of occurrence of lethal and sterile mutation within the same stock and experiment. The data are summarized in the table.

Rate of Spontaneous Mutation in *D. melanogaster*

| | Lethal mutations | | | Sterile mutations | | |
|---|---|---|---|---|---|---|
| | *X*-chromosome | II chromosome | III chromosome | *X*-chromosome | II chromosome | III chromosome |
| Number of studied chromosomes | 5201 | 3132 | 1446 | 3049 | 2841 | 812 |
| Number of mutations | 13 | 18 | 8 | 1(+1?)* | 1 | 0 |
| Percentage of mutations | 0.25 | 0.57 | 0.55 | 0.03(0.06?) | 0.03 | 0 |
| Comparative frequency of mutations | 1 | 2.3 | 2.2 | — | — | — |

The data presented above should be discussed from different points of view.

I. Up to the present day no data have ever been published on the natural rate of occurrence of steriles. According to our data, the frequency of occur-

* In this case only 3 males have been studied for sterility; they were taken from one $F_2$ culture and brought together with 6 virgin females. Within the first 24 hours 2 males died. The male which survived lived 3 days during which it has been twice transferred together with the females to fresh food. It gave no progeny.

rence of steriles in the *X*-chromosome is equal to 0.03%. The value obtained fails, however, to fully characterize the rate of sterile mutations arising in the *X*-chromosome. Besides steriles acting in males, there arise those acting in females, too. According to the data now available, there are about as many female steriles as male in the *X*-chromosome ([3]). Assuming that the frequency of sterile mutations is equal for both types, we may obtain the approximate value of the general rate of steriles arising in the *X*-chromosome by doubling value characterizing the frequency of male sterile mutations. The same assumption holds true for the autosomes where the general frequency of sterile mutations will be twice as great as the rate found by us for female steriles.

Assuming that within a single generation there arises in the III chromosome as many steriles as in the II chromosome [we have ground to suppose it, since the number of steriles found in the II and III chromosomes is about the same ([3])], we find that about 0.18% of sterile mutations arises pro gameto-generation. This value is of course only approximative. The data obtained show therefore a relatively high frequency of spontaneous sterile mutations. However, the frequency of occurrence of lethal mutation is still considerably higher.

II. The data obtained enable us to discuss as well the question of the relative frequency of spontaneous mutation in individual chromosomes. According to the data presented in this paper, the relative frequency of mutation in the *X*, II and III chromosomes may be expressed by the following figures: 1 : 2.3 : 2.2, respectively. Let us now compare the ratio obtained with the one established for X-ray mutations. Data on the relative mutability of X-rayed chromosomes have been collected and partly published by us previously ([1,2]). On the basis of these investigations the ratio of mutations was found to be equal to 1 : 2.6 : 2.8. It may be seen that data on spontaneous mutations do not differ materially from those on X-rays mutations.

Comparing the relative frequency of mutation in individual chromosomes with their lengths, in one of our previous papers we came to the conclusion that the frequency of mutation is in proportion with the length of the active regions of chromosomes ([1]). Later on other writers have also joined this conclusion ([4,5]). Comparing the relative frequency of spontaneous mutations in different chromosomes with the length of their active regions, we have to point out a considerable coincidence of these values. The ratio of active regions of the sex-chromosome to active regions of autosomes is 1 : 2 : 2.2, respectively. The ratio of the length is even somewhat closer to the ratio characterizing the spontaneous mutation rate than the ratio for X-rays mutations. Taking into account the error both in determining the length of active regions and of the mutation rate, the high degree of coincidence of the values compared becomes obvious.

It is, however, necessary to point out that in a series of experiments ([1,2,6]) there is a somewhat disproportional increase of mutability of the autosomes as compared to the sex-chromosome. This fact has given ground to one of the authors working on this problem ([6]) to assume that this disproportionally high mutability of autosomes was no matter of chance, but was due to a greater stability of genes contained in the sex-chromosome. Without denying the possibility (although taking not it for proved either) of a somewhat greater frequency of lethal mutations per unit length in the autosomes as compared to the sex-chromosome, we believe it wrong to refer this phenomenon to a greater mutability of autosomal genes.

According to the assumption suggested by us in a previous paper ([7]), the evolution of mutability for all chromosomes (the autosomes as well as the sex-chromosome) proceeded in the direction from higher to lower mutability. No doubt, the *X*-chromosome occupies a specific place among other chromoso-

mes (heterogamety of males). This specificity leads to the increase in the detrimental effect of mutation process which proceeds in the sex-chromosome as compared to the autosomes (assuming the possibility of somatic mutations in the heterogametic sex). Nevertheless, the harmful effect of mutability of the *X*-chromosome, leading in *D. melanogaster* chiefly to the elimination of males, is perhaps less harmful to the species than mutability of autosomes, leading to the elimination of both sexes (Serebrovsky). Heterogamety of the one of the sex undoubtedly ensures a more rapid rate of selection for low mutability in sex-linked genes as compared to autosomal genes; however, inasmuch as the evolution of mutability for lower rates is a process which has a long history, it is obvious that difference in mutability between sex-chromosomes and autosomes should have become levelled to the present moment. The specific condition of the *X*-chromosome could perhaps have influenced only the efficiency of selection for low mutability per unit time. It would be perhaps possible to expect a greater variability of mutation rate in the autosomes as compared with the *X*-chromosome. But this seems to us scarcely probable. We believe that the genotypical control of the mutation rate is realized chiefly through the selection of modifiers influencing both sex-linked and autosomal genes simultaneously. This assumption is supported by the fact that all the modifiers of mutability known at the present time for *Drosophila* and other organisms influence the general mutability of all (not individual) chromosomes ([8-12]). The supposed decrease of the number of lethals mutations in the *X*-chromosome may be explained, according to Berg's data ([6]), by assuming that the *X*-chromosome contains genes whose mutations give no lethal allelomorphs (for instance, genes of sex and of productivity).

III. In conclusion let us consider the mutability of the entire genome of *D. melanogaster*. According to the data presented above, the proportion of lethals arising per gameto-generation is equal to 1.37%. This experimental value is very close to that previously calculated by us with the aid of another method ([7]). On the basis of literary data embracing a great number of experiments in which over 100 000 sex-chromosomes were investigated, we have calculated the mean frequency of production of sex-linked lethals and obtained the value 0.23%. Having taken from X-ray experiments the relative frequency of mutation in individual chromosomes, we have established the frequency of the spontaneous mutation of the genome as a whole. This frequency was equal to 1.5%. Considering the nature of the method used (the mean frequency of mutation in the sex-chromosome being taken as the initial point of calculation), the figure obtained characterizes the mean frequency of lethals arising in the genome. The frequency of lethal mutations obtained in the experiment is therefore very close to the mean frequency. Together with lethal mutations there arise semilethals and mutations but slightly affecting viability. According to different data ([13,14]), the number of mutations reducing viability, without being entirely lethal, is about thrice as great as the number of lethals. Hence, on the basis of the number of lethal mutations found in our experiment we may assume that the whole number of viability reducing mutations which arise in the genome per gameto-generation should be equal approximately to 5.48%.

It has been found by us that there arise about 0.18% steriles per one gameto-generation. Assuming that together with steriles there arise as well mutations reducing fertility and that their number is 3 times as great as the number of steriles (by analogy with lethals), we obtain the value 0.72% of mutations reducing fertility which arise per gameto-generation. Summing up the percentages of viability and fertility mutations, we obtain the figure of 6.20%. The thus obtained percentage of mutations arising per gameto-generation is somewhat lower than the true frequency of mutation. This is due to the

fact that the mutability of the IV chromosome has not been studied by us, as well as the frequency of some categories of mutations was omitted, too (such as visible mutations, dominant lethals and steriles and others).

All the figures and calculations given in the present work characterize only the given stock of *D. melanogaster*. It has been shown above that in respect to the frequency of mutation this stock is very close to the assumed standard mutability peculiar to the species. Lately a series of papers have been published by different authors describing stocks of *D. melanogaster* showing a very high mutability ([9-12]). These cases are undoubtedly of very great interest for the analysis of the mechanism of spontaneous mutations. The value of these lines for the study of normal natural mutation rate is, however, much smaller. While demonstrating the possible variability of the species in respect to mutation rate these stocks represent pathological deviations from the standard.

In the paper ([7]) already cited above we supported the view that in the course of evolution there was selection for low mutability and that this selection is still going on maintaining the low level of mutability. The necessity of this selection is demonstrated by the continuous occurrence of mutations increasing the mutation rate. Being deleterious, these mutations are eliminated by selection. In this respect the mutation rate does not differ from any other genotypically controlled property of the organism.

Accepting this point of view, the characteristics of mutation rate of a species and all calculations connected with the frequency of mutation must be based on data obtained from the study of stocks whose rate of mutation is close to the standard rate of the species. The study of stocks showing high mutability may be necessary for the investigation of some special problems only.

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*GENETICS*

# ON THE FATE OF X-RAY MUTATIONS OCCURRING IN SPERMATOZOA WHEN KEPT IN THE SPERMATHECA OF THE FEMALE

By N. I. SHAPIRO

*(Communicated by I. I. Schmalhausen, Member of the Academy, 20. VI. 1939)*

Nearly at the same time in 1937 two papers were published containing data on the behaviour of lethals arisen in X-rayed spermatozoa of *D. melanogaster* kept afterwards in the spermatheca of the female ([1],[2]). Experimental data and conclusions of these works proved contradictory.

Since the method used by us in a series of experiments is based on the assumption that lethals arisen in spermatozoa are preserved when ageing in the female's spermatheca ([3]), we were highly interested to find out the real state of things.

We were interested, in the first place, to know whether or not there is a decrease in the frequency of lethal mutations when X-rayed spermatozoa are kept. Such a decrease may be expected if we admit the existence of germinal selection, i. e. in case lethal mutations lead to the destruction of spermatozoa, the lethal effect being gradual.

At the present time a series of experimental works are known which show that various lethal mutations and chromosomal aberrations which kill the zygote do not function in the spermatozoa ([4],[5],[6]). This is supported by every day experience of anyone who is working on lethal mutations.

If lethal mutations of *D. melanogaster* were active in gametes, we either would never discover this category of mutations (in case lethals came to expression in 100% of gametes), or would witness the disturbance in mendelian ratios of lethal mutations (in case there were no 100% expression in gametes). Inasmuch as inheritance of lethals in *D. melanogaster* does not differ from that of any other character, we have no ground to suppose that lethals which kill the zygote produce a similar gametic effect. Thus, data so far available give evidence against the assumption of germinal selection among spermatozoa. The inactivity of the genes in the spermatozoa is evidently an adaptive property which is acquired in the course of evolution. However, this should not be taken to mean that there are no mutations able to change the morphological and physiological properties of the gametes. They certainly do exist. Nachtsheim ([7]) might possibly have succeeded in detecting one of such mutations (affecting the duration of life of spermatozoa in *D. obscura*). Most probably, such mutations are of rather rare occurrence; at any rate, neither lethals nor chromosomal aberrations usually observed affect in the great majority of cases the viability of spermatozoa.

All these data and arguments made us very cautious with regard to materials, in which a decrease in the frequency of detection of lethal mutations was observed in spermatozoa kept in spermatheca. We did not, however, find it possible to reject such a possibility merely on the ground of the evidence previously produced.

Two series of experiments were arranged in this connexion. In each of them fertilized *ClB* females were X-rayed and divided in two groups, one of which was analyzed immediately, the other 15 days upon treatment. The frequency of sex-linked lethal mutations was established. The results of these experiments are summarized in the table below.

Effect of Keeping X-rayed Spermatozoa on the Frequency of Mutations Found in *D. melanogaster*

| Series № | Dosage, *r* | Duration and conditions of keeping X-rayed spermatozoa | Number of the $F_2$-cultures studied | Number of lethal mutations found | % of lethals found |
|---|---|---|---|---|---|
| I | 2400 | Not kept . . . . . | 165 | 11 | 6.67 |
| | | Kept for 15 days at 21—22°C | 187 | 18 | 9.63 |
| II | 1200 | Not kept . . . . . | 777 | 29 | 3.74 |
| | | Kept for 15 days at 22—23°C | 448 | 19 | 4.24 |

As may be seen from the table, the frequency of lethals found in spermatozoa after their keeping is by no means lower than that in spermatozoa used immediately upon treatment.

Our data are thus in full accord with those of Muller and Settles, Harris and Kühn ([4,5,6]). Our material points even to some increase in the mutation rate in spermatozoa after keeping.

This increase cannot be regarded as statistically significant [the same as in the work by Sitko ([2])]. When the study will be extended over a larger number of chromosome, the increase in the frequency of mutations in spermatozoa after keeping may prove to depend not on a mere chance. This increase should be anticipated, if one assumes the existence of a certain after-affect of X-rays upon the mutation process, i. e. that a fraction of mutations arises not at the very moment of treatment, but somewhat later. The latter problem will constitute the subject of a special study.

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*GENETIK*

# ERZEUGUNG VON TETRAPLOIDEN PFLANZEN BEIM HANF DURCH COLCHICINBEHANDLUNG

Von W. A. RYBIN

*(Vorgelegt von N. I. Vavilov, Mitglied der Akademie, d. 14. VI. 1930)*

Bei meinen Experimenten zwecks Erzeugung von Tetraploiden nach der Methode von Blakeslee (1) wählte ich als Versuchsobjekt den Hanf aus folgenden Gründen. Die Anwendbarkeit der Balancetheorie der Geschlechtsbestimmung auch in betreff pflanzlicher Objekte ist in letzter Zeit besonders eingehend in der Arbeit von Yamamoto (2) mit Sauerampfer dargelegt worden, infolgedessen unterliegt es keinem Zweifel, dass die auf experimentellem Wege herworgerufene Polyploidie bei dem Hanf als Begleiterscheinung das Entstehen von Intersexen aufweisen würde. Zweifellos wird die Möglichkeit der Erzeugung von genotypisch zwitterigem Hanfe ein grosses theoretisches und vielleicht auch praktisches Interesse bieten.

Die Versuche wurden mit 2 Hanfmustern: 1) Nowgorod-Ssewersky (Detskoe Sselo, geerntet 1937), 2) Italienischer 1797*, angestellt; beide von der Abteilung für technische Kulturen des Instituts für Pflanzenbau bezogen.

Nachdem die Pflanzen eine Höhe von 20—30 cm erreicht, und ein Paar einfacher, sowie zwei Paare zusammengesetzter Blätter ausgebildet hatten, wurden sie auf 24 Stunden in eine 0.05—0.1% wässrige Lösung von Colchicin getaucht. Vor dem Eintauchen in die Lösung wurden sowohl die einfachen Blätter, wie auch die zusammengesetzten mit einer Schere ungefähr um $^1/_3$—$^1/_2$ ihrer Länge gekürzt, um dadurch das Eindringen des Colchicins in das Pflanzengewebe zu erleichtern. In keinem einzigen Fall rief das Eintauchen in Colchicin ein Eingehen der Pflanzen hervor.

Ungefähr in 18—20 Tagen nach dem Eintauchen der Versuchspflanzen in Colchicin konnten an ihnen charakteristische Veränderungen beobachtet werden (Abb. 1).

Die Triebe hatten eine dunklere Färbung angenommen, die Fiederblättchen des zusammengesetzten Blattes schienen etwas wie zerknittert, hatten unregelmässig gezahnte Blattränder, öfters eine unsymmetrische Entwicklung der rechten und linken Blatthälfte und eine etwas weniger glänzende mattere Blattfläche. An den Stellen der Abzweigung der Seitensprossen konnten eigentümliche Anschwellungen beobachtet werden, die ihrem Aussehen nach an eine Kallusbildung erinnerten. Öfters waren die Seitentriebe im Durchmesser 2—3 mal dicker als der Hauptstengel. Die Quer- und Flächenschnitte von Blattspreiten der veränderten Blätter wiesen darauf hin, dass

* Beide Muster wurden mir von N. A. Belowitzkaja verschafft, wofür ich ihr an dieser Stelle meinen besten Dank ausspreche.

im Vergleich zu den normalen Blättern dieselben: 1) eine dickere Blattspreite, 2) grössere Zellen des Palisadenparenchyms, 3) grössere Haaren- und Schliesszellen der Spaltöffnungen besassen*.

In dem vorliegenden Aufsatz werde ich mich eingehender nur mit einem Paar von Versuchspflanzen des Nowgorod-Ssewersky Hanfes im Topf Nr. 1 befassen, da gegenwärtig nur von ihnen tetraploide Nachkommen herangezogen worden sind; die Samen der übrigen Versuchspflanzen sind noch nicht ausgesät.

Abb. 1. Pflanzen des Italienischen Hanfes, verändert durch die Einwirkung von Colchicin (links), Kontrollpflanzen (rechts).

Die männliche Pflanze im Topf Nr. 1 blühte vor der weiblichen, hatte im Vergleich zu den Kontrollpflanzen grössere Blüten und grösseren Pollen, der aus einem Gemenge von normalen und grösseren Pollenkörnern bestand. Die weibliche Pflanze blühte 40 Tage später, während dieser Zeit blühte die männliche Pflanze des Nowgorod-Ssewersky Hanfes im Topf Nr. 10. Beide Pflanzen dieses Topfes, sowohl die männliche, wie die weibliche, wiesen typische Kennzeichen der Einwirkung von Colchicin auf. Die weibliche Pflanze Nr. 1 wurde unter die männliche Pflanze, die sich in voller Blute befand, gestellt. Keine der Pflanzen wurde isoliert, so dass der Pflanze Nr. 1 die Möglichkeit gegeben wurde, teilweise mit Pollen anderer Versuchs- und Kontrollpflanzen, die am gegenüberliegenden Ende des Gewachshauses blühten, bestäubt zu werden. Nach 18 Tagen war die Blütezeit der Pflanze Nr. 1 beendet und eine beträchtliche Anzahl von Samen angesetzt. Die Samen wurden nicht auf einmal gesammelt, sondern je nach ihrem Ausreifen. Dabei wurde bemerkt, dass die Samenkörner der Pflanze Nr. 1 sich stark nach der Grösse unterschieden, die Samenkörner des Hauptstengels und seiner kleinen Seitensprosse waren zweimal so gross, wie die Samenkörner der beiden Seitentriebe (Abb. 2). Solch ein auffallender Unterschied in der Grösse der Samenkörner

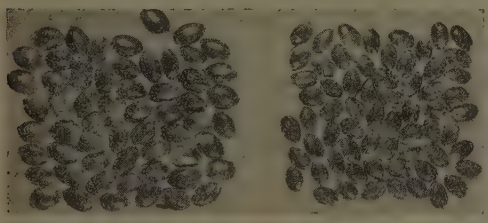

Abb. 2. Samenkörner des Nowgorod-Ssewersky Hanfes: 1) von den Seitentrieben (links), 2) vom Hauptstengel (rechts).

* Blakeslee und Warmke empfehlen zum Nachweis von polyploiden Trieben, an den weiblichen Hanfpflanzen, bei denen keine Möglichkeit vorhanden ist, weder die Grösse der Pollenkörner zum Vergleich heranzuziehen, noch die Meiosis in den Antheren mit dem Acetokarminverfahren zu erforschen, die anatomischen Elemente der Deckblätter zu vergleichen.

legte den Gedanken nahe, dass die Pflanze Nr. 1 eine Chimäre darstellte, bei der der Hauptstengel mit seinen kleinen Seitensprossen aus einem Gewebe besteht, das sich nach der Zahl der Chromosomen von den beiden Seitentrieben unterscheidet. Zur Prüfung dieser Annahme gab ich noch vor dem Frühjahr 6 grossen Samenkörnern, die ich vom Hauptstengel gesammelt hatte und weiterhin als Spross *D* bezeichnen werde, und 6 kleinen Samenkörnern der beiden Seitentriebe *B* und *C* die Möglichkeit auszukeimen. Die zytologischen Untersuchungen der Hauptwürzelchen der 5 Sämlinge des Sprosses *D* (die Wurzel des 6-ten Sämlings wurde zufällig nach dem Fixieren beschädigt) und der 6 Sämlinge der Triebe *B* und *C* ergaben, dass alle 6 Sämlinge der Triebe *B* und *C* 20 Chromosomen aufwiesen, während die 5 erforschten Sämlinge des Sprosses *D* die tetraploide Zahl besassen. Bei der Durchsicht der Präparate bestätigten sich die Angaben von Litardière (4), der als erster darauf hingewiesen hatte, dass im Periblem der Wurzelspitze des Hanfes eine bedeutende Anzahl von Zellen zu beobachten sei, in denen die Anzahl der Chromosomen das doppelte des Chromosomensatzes in den Zellen des Pleroms betrage. Es ist der Beachtung wert, dass dieselbe Gesetzmässigkeit von mir auch bei den tetraploiden Pflanzen nachgewiesen wurde. Bei den letzteren hatten die meisten Zellen des Periblems die oktoploide Chromosomenzahl, nämlich 80. Tetraploide Platten bei den diploiden Pflanzen und oktoploide bei tetraploiden wurden vom mir im Plerom beobachtet, aber in verhältnismässig geringer Anzahl, was mit den Ergebnissen, die Litardière bei der Erforschung des diploiden Hanfes erhalten hatte, übereinstimmt.

Zwei Sämlinge des Sprosses *D* und einer der Triebe *B* und *C* gingen zufälligerweise im Stadium der ersten zwei Blätter ein, die übrigen 4 tetraploiden und 5 diploiden Pflanzen wurden bei elektrischer Belichtung im Laboratorium für Licht-Physiologie des Physikalisch Agronomischen Instituts herangezogen*. Alle 4 tetraploiden Pflanzen erwiesen sich als weibliche, unter den 5 diploiden befanden sich aber 2 männliche und 3 weibliche.

Die bei elektrischer Belichtung herangezogenen Hanfpflanzen kennzeichneten sich durch schwache Belaubung und verlängerte Internodien (Abb. 3). Die tetraploiden Pflanzen unterschieden sich von den diploiden durch das Verhältnis zwischen der Länge und Breite der Fiederblättchen des zusammengesetzten Blattes: bei tetraploiden war das Verhältnis der Breite zur Länge ein grösseres. Die Zellen der Epidermis, des Palisaden und Schwammparenchyms, sowohl wie die Haaren waren bei den Tetraploiden bedeutend grösser. In Hinsicht der generativen Entwicklung waren die bei elektrischer Belichtung herangezogenen Pflanzen vollkommen normal. Die Erforschung der Meiosis in den Antheren der diploiden Pflanzen *BC*-5 mit Hilfe von Acetokarmin, zeigte die Regelmässigkeit der ersteren. In den Metaphasen der heterotypischen Teilung wurden in allen Fällen 10 Bivalente nachgewiesen. Der Pollen der beiden diploiden Pflanzen hatte normale Form und Grösse, er keimte gut in Zuckerlösung.

Da unter den tetraploiden Pflanzen** keine männliche vorhanden waren, mussten sie mit Pollen der diploiden Pflanzen *BC*-1 und *BC*-5 bestäubt werden.

---

* Bei dieser Gelegenheit möchte ich Herrn Prof. Maltschewsky, Leiter des Laboratoriums, der mir die Möglichkeit verlieh das Gewächshaus des Laboratoriums zu benutzen, meinen tiefempfundenen Dank erstatten, sowie meine grosse Erkenntlichkeit S. I. Dobrochotowa für die mir beim Heranziehen der Pflänzlinge geleistete Hilfe.

** Es ist bemerkenswert, dass eine von den tetraploiden Pflanzen (*D*-3) in der Vollblüte eine geringe Anzahl von männlichen Blüten ausbildete, die sich als einzelne Blüten oder als mehrere Blüten zusammen inmitten der weiblichen Blüten befanden. Trotz des normalen Aussehens des Pollens der Pflanze *D*-3 keimte er nicht in der Zuckerlösung.

Infolge einer solchen Bestäubung setzten alle 4 tetraploiden Pflanzen eine beträchtliche Anzahl Samen an. Die Samenkörner der tetraploiden Pflanzen waren viel grösser als diejenigen der diploiden (Abb. 4), und da der Bestäuber eine diploide Pflanze war, sollen alle Samen ein triploider Chromosomensatz besitzen*.

Von den übrigen Pflanzen werde ich mich hier nur mit zwei Pflanzen des Hanfes Nowgorod-Ssewersky im Topf Nr. 6 beschäftigen. An diesen beiden Pflanzen machte sich das Eintauchen derselben in eine Colchicinlösung ganz besonders bemerkbar. Die männliche Pflanze blieb stark im Wachstum zurück

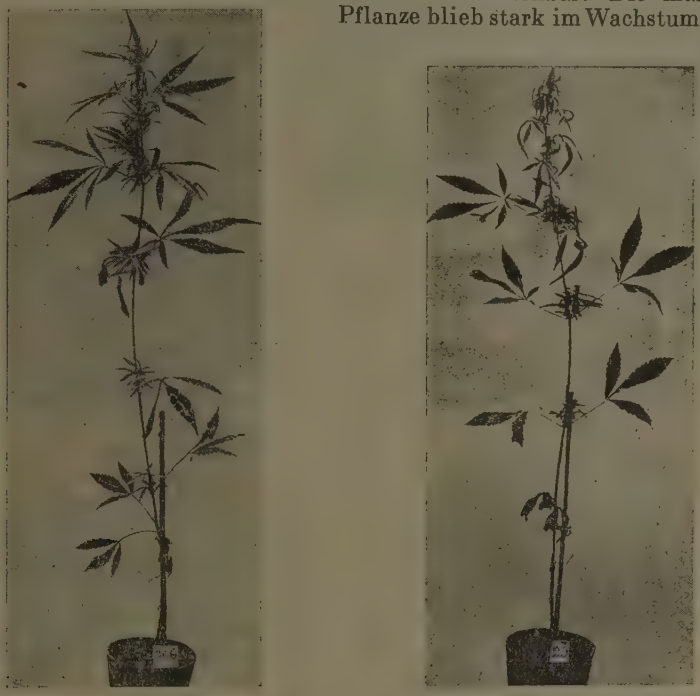

Abb. 3. Weibliche Hanfpflanzen, herangezogen bei elektrischer Belichtung: 1) tetraploide Pflanze *D*-3 (links), 2) diploide Pflanze *BC*-6 (rechts).

und stellte ein Zwerggewächs mit einer Höhe von etwa 30 cm dar. Ihre Blätter unterscheiden sich durch dunkelgrüne und verkümmerte Blattspreiten. Die Pflanze entwickelte eine geringe Anzahl äusserst missgestalteter Blüten. Die Antheren der letzteren waren stark deformiert und wiesen Auswüchse auf, die ihrer Form nach an verkümmerte Narben erinnerten**. Mit Hilfe einer Nadel konnte aus den Antheren der Pollen herauspräpariert werden. Das Quantum war nicht gross. Die Pollenkörner unterschieden sich durch ihre ungewöhnliche Grösse, sie waren 3—4 mal grösser als die normalen. Unter den grossen Körnern befanden sich im Gemenge auch kleinere. Die weibliche

* Theoretisch ist anzunehmen, dass sich unter den Sämlingen von dieser Bestäubung Intersexe mit einem Satz *XXY* befinden müssen.

** Hier weise ich darauf hin, dass die Blüten der männlichen Pflanzen im Topf Nr. 6 sehr stark der Abbildung von missgestalteten Zwitterblüten in der Arbeit von Correns (5), die er der Arbeit Schaffners entnommen hatte, ähnelten.

Pflanze war gleichfalls in der Entwicklung zurückgeblieben und missgestaltet. Der Hauptstengel war abgestorben, statt seiner hatten sich zwei starke und einige schwächere Seitentriebe entwickelt. Die letzteren trugen stark deformierte Blätter mit sehr unregelmässigen Fiederblättchen. Die Pflanze unterschied sich durch eine sehr dunkle Färbung der Blätter und durch eine ums doppelte verminderte Höhe. Sie blühte später als alle übrigen Versuchspflanzen, und da kein Ansetzen der Samen zu erkennen war, obgleich die Pflanze ohne Isolierung in einer Gruppe mit anderen Pflanzen zusammen gestanden hatte, wurde auf diese Pflanze während einiger Tage nacheinander Pollen von Versuchspflanzen des Italienischen Hanfes Nr. 7 und 8 abgeschüttelt. Die beiden letzteren Pflanzen hatten sehr grosse Pollenkörner, die ums doppelte die Kontrolle übertrafen. Beim Absammeln der Samen von der Pflanze Nr. 6 erwies es sich, dass die meisten Früchte keine Samen enthielten, nicht pigmentiert waren, und ihrer Grösse nach variierten. Dennach gelang es von den missgestalteten Trieben einige Dutzend normal entwickelter sehr grosser Samenkörner zu sammeln. Dieselben übertrafen ihrer Grösse nach die tetraploiden Samenkörner des Sprosses *D* der Pflanze Nr. 1 (Abb. 5). Bei Durchsicht der Schnitte durch die Blattfläche der Blätter von den missgestalteten Trieben der Pflanze Nr. 6 erwies es sich, dass die Epidermis mit sehr grossen Haaren bedeckt war, die um das drei oder vierfache die Haaren der Kontrollpflanzen übertrafen. Sehr grosse Ausmasse hatten auch die Schliesszellen der Spaltöffnungen.

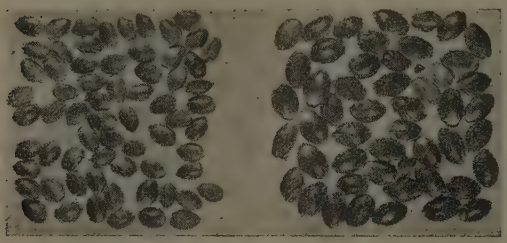

Abb. 4. Samenkörner der Nowgorod-Ssewersky Hanfpflanzen, herangezogen bei elektrischer Belichtung: 1) der diploiden Pflanze (links), 2) der tetraploiden (rechts).

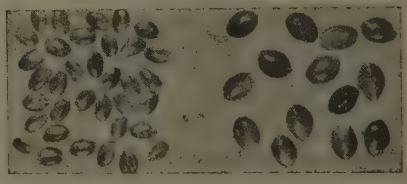

Abb. 5. Samenkorner des Nowgorod-Ssewersky Hanfes: 1) des diploiden Triebes der Pflanze Nr. 1 (links), 2) des Triebes der Pflanze Nr. 6 verändert durch Einwirkung von Colchicin (rechts).

Die verminderte Fruchtbarkeit, die ums drei-vierfache die Norm übertreffende Grösse der Samenkörner und die im Vergleich mit den Kontrollpflanzen sehr grossen Haare und grossen Spaltöffnungen erwecken den Gedanken, dass die missgestalteten Triebe der Pflanze Nr. 6 nicht einen tetraploiden, sondern einen oktoploiden Chromosomensatz haben.

Bei den vier erhaltenen tetraploiden Pflanzen blieb das Geschlecht unverändert*. Eine Veränderung des Geschlechts wurde bei den von Blakeslee und Warmke ([3]) erhaltenen tetraploiden Hanfpflanzen auch nicht beobachtet, ebenso wie bei den zehn von Westergaard ([7]) erhaltenen tetraploiden Pflanzen von *Melandrium album*. Blakeslee ([8]) erhielt beim Hanf auch eine tetraploide $F_2$, doch über die Ausprägung des Geschlechts bei den Pflanzen dieser Generation wird in der angeführten Arbeit von dem Verfasser nichts bekannt gegeben.

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* Nach den Angaben von Hirata([6]) wird das Geschlecht beim Hanf nach dem *XY* Typ vererbt. Heterogametisch ist das männliche Geschlecht.

Die hier angegebenen Tatsachen erlauben folgende Schlussfolgerungen: 1) Bei Einwirkung von Colchicinlösungen auf junge Hanfpflanzen entstehen bei den letzteren leicht Triebe mit polyploidem Chromosomensatz. 2) Die veränderten Triebe sind leicht nach ihrem äusseren Habitus, der Grösse der Pollenkörner, der Dicke der Blattspreiten und den Ausmassen der anatomischen Elemente des Blattes, nämlich der Haare, der Schliesszellen, der Spaltöffnungen, der Zellen des Palisadenparenchyms, zu erkennen. 3) Die tetraploiden Triebe weisen keinerlei verminderte Fruchtbarkeit auf, die Samenquantität ist normal. 4) Es wird eine bestimmt positive Korrelation zwischen der Chromosomenanzahl und der Grösse der Samenkörner beobachtet: die tetraploiden Samenkörner sind zwei-drei mal grösser als die diploiden. 5) Ausser tetraplöiden Trieben entstehen scheinbar an den Pflanzen, die einer Einwirkung von Colchicin unterzogen wurden, auch Triebe mit einer noch grösseren Chromosomenzahl.

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*GENETICS*

# A BIOCHEMICAL METHOD OF LARGE SCALE ESTIMATION OF PRUSSIC ACID IN SORGHUM FOR BREEDING PURPOSES

By M. I. SMIRNOVA and G. A. KATANSKAJA

*(Communicated by N. I. Vavilov, Member of the Academy, 13. VI. 1939)*

Sorghum is a highly valuable crop as regards its physiological and chemical characters, but it stores up considerable amounts of glucoside which yields prussic acid on hydrolysis ([1]—[3]).

On the basis of works carried on during the latter six years in this laboratory ([4], [5], [6], [7]) as well as abroad ([8], [9]) many biochemists and plant-breeders have been striving to obtain non-poisonous and non-bitter forms by means of selection. In that way, too, the authors of the present paper were induced to breeding for sorghum varieties low in cyanide. Should they succeed in obtaininig forms practically deprived of cyanide, the plant will become an important item in the diet of the live stock in droughty areas.

The first experiments along that line, started in 1935—1936, showed the various varieties of sorghum grown under the conditions of the experimental station Otrada Kubanskaya (North Caucasus) to vary greatly in their content of hydrocyanic acid. Thus, according to Safronov, the leaves of the varieties enumerated below showed the following amount of hydrocyanic acid at the time when panicles started growing. Estimation was made according to Liebig. Percentage of hydrocyanic acid reported on a dry-matter basis is:

*Minnesota Amber* 0.079%, *Orange* 0.128%, *North Caucasus* 0.208%.

Further breeding for cyanide low forms was conducted by way of individual selection. This, in turn, required that a new method should be devised to make rapid estimation of hydrocyanic acid possible. Among the quantitative and qualitative micromethods available for determination of this acid in a biological material we have chosen the method of Guignard ([10], [11]) and made also use of the data reported by François et Laffitte([12]). Guignard's method of picrate paper is based on the influence of the hydrocyanic upon the picric acid which it converts into purpuric acid.

A wet strip of picrate paper is let to hang in the air where the vapour of hydrocyanic acid is supposed to be present. If it is actually so, the paper will change its original green-yellow colour into orange-red. The higher the available amount of hydrocyanic acid, the more red will the paper look. The paper responds to as low an amount of HCN in the air as 0.005 mg per litre. This highly sensitive, simple and rapid technique is quite suitable for large scale analyses and selection of individual sorghum plants low in cyanide.

The estimation of hydrocyanic acid was made as follows. 1 g aliquot of leaves was quickly grounded with glass and some few drops of toluene in a porcelain mortar. The mass obtained was placed in a graduated flask and made up to 100 cm³ by adding water. The flask was corked tightly, allowed to stand at room temperature for 12 hours. While it was standing the extraction and splitting up of glucoside was taking place in it and the hydrocyanic acid was partly liberated. Afterwards the contents of the flask was thoroughly stirred and 5 cm³ suspension were taken off into a conical flask 60 mm high and 20 mm broad at the bottom. The flask was tightly closed with a cork which had a strip of reaction paper (4 mm × 30 mm) sticking on it by means of paraffin. There it was kept in the dark at room temperature during 48 hours. Two flasks were loaded by each of the samples. The intensity of the colour taken on by the paper was the measure to estimate the content of hydrocyanic acid quantitatively. This was done against a standard scale of colours produced by the respective amounts of HCN in a sample.

The scale was a set of flasks filled with KCN solutions acidulated with tartaric acid. The solutions were prepared from water and an initial solution of KCN blended in varying proportions and making up a volume of 5 cm³. The initial solution contained 10 mg KCN per 200 cm³.

Table 1

| Scale No. | Initial solution of KCN, cm³ | $H_2O$ cm³ | HCN mg |
|---|---|---|---|
| 1 | 5.00 | 0.00 | 0.103 |
| 2 | 4.50 | 0.50 | 0.093 |
| 3 | 4.00 | 1.00 | 0.083 |
| 4 | 3.50 | 1.50 | 0.073 |
| 5 | 3.00 | 2.00 | 0.062 |
| 6 | 2.50 | 2.50 | 0.052 |
| 7 | 2.00 | 3.00 | 0.042 |
| 8 | 1.50 | 3.50 | 0.031 |
| 9 | 1.00 | 4.00 | 0.021 |
| 10 | 0.80 | 4.20 | 0.017 |
| 11 | 0.60 | 4.40 | 0.012 |
| 12 | 0.50 | 4.50 | 0.010 |
| 13 | 0.40 | 4.60 | 0.008 |
| 14 | 0.30 | 4.70 | 0.007 |
| 15 | 0.25 | 4.75 | 0.005 |
| 16 | 0.20 | 4.80 | 0.004 |
| 17 | 0.15 | 4.85 | 0.003 |
| 18 | 0.10 | 4.90 | 0.002 |
| 19 | 0.05 | 4.95 | 0.001 |
| 20 | 0.00 | 5.00 | 0.000 |

The way of determination was to find in the scale the flask nearest in colour to the test flask and its respective content of HCN in mg was that

Table 2

Content of Hydrocyanic Acid in Leaves of Various Sorghum Varieties at the Time of Panicle Formation in 1937 (mgs per 100 g of raw material)

| Catalogue No. | Variety | Range of HCN content | Average | Number of specimens analyzed |
|---|---|---|---|---|
| 279 | *Frid Sorghum* | 10—125 | 62 | 59 |
| 395 | *Early Amber* | 6—125 | 42 | 66 |
| 813 | *China Amber* | 4—69 | 27 | 24 |
| 150 | *Red Amber* | 17—125 | 46 | 46 |
| 163 | *Early Honey*, awnless | 12—83 | 30 | 53 |
| 310 | *Intermediate Honey* | 0—143 | 42 | 38 |
| 201 | *McLean Sorgo* | 14—95 | 28 | 44 |
| 326 | *Orange* | 2—42 | 23 | 47 |
| 247 | *Sanraiz Kafir* | 1—28 | 13 | 59 |
| 1559 | *Gaolan red* | 10—104 | 36 | 37 |
| 799 | » *local* | 17—125 | 62 | 37 |
| 514 | *Gaolan* | 12—125 | 33 | 39 |
| 1037/A | *Gaolan* | 12—125 | 42 | 60 |
| 769 | *Dhurra* from Palestine | 3—42 | 23 | 10 |
| 549 | *Brown Dhurra* | 17—42 | 27 | 50 |
| 1543 | *Dhurra* from Palestine | 14—95 | 28 | 27 |

sought. The amount of CHN thus established was expressed in mgs per 100 g of initial substance. The picrate paper method gave concordant results when compared to the qualitative method of Liebig.

The investigation involved the sorghum varieties making up the collection of this Institute. The material to be tested was grown at the experimental station Otrada Kubanskaya in 1937—1938.

On analyzing the leaves of the various plants we found that all varieties are not alike in their ability of storing up hydrocyanic acid. The leaves were always taken from the third or the fourth upper node.

The tabulated data show that the average content of hydrocyanic acid in the 16 varieties tested varies between 13 and 62 mg/% and the range of variation is still wider if individual plants are considered. In several cases against equal average amounts of hydrocyanic acid we find varieties which exhibit varying degrees of plasticity in this particular and only some of them can be used successfully in breeding forms low in cyanide. This is illustrated clearly by an extract from Table 3.

Table 3

| Variety | Range of HCN content mg/% | Average |
|---|---|---|
| *Orange* | 2—42 | 23 |
| *China Amber* | 4—69 | 27 |
| *Dhurra* from Palestine | 3—42 | 23 |
| *Brown Dhurra* | 17—42 | 27 |
| *Dhurra* from Palestine | 14—95 | 28 |
| *McLean Sorgo* | 14—95 | 28 |

On the basis of the data obtained in 1937 we selected a set of cyanide-low plants. The seeds of those plants were planted at the same station in 1938. The test for hydrocyanic acid took place in summer at the time when panicles started formation.

From the figures in Table 4 it will be obvious that we were right in taking account of the data on individual plants, since the forms we had chosen among the harvest 1937 preserved their character in the harvest 1938.

Table 4

Variation of HCN Content in Leaves of Certain Lines within Variety *Orange 326*

| Line No. | Percentage of HCN in raw weight of leaves | | | | Number of specimens tested in 1938 |
|---|---|---|---|---|---|
| | Strains from harvest 1937 | Harvest 1938 | | | |
| | | Minimum | Maximum | Average | |
| 4 | 2 | 0 | 16 | 6.2 | 6 |
| 5 | 8 | 2 | 12 | 7.6 | 9 |
| 6 | 10 | 0 | 16 | 9.2 | 26 |
| 11 | 10 | 4 | 24 | 11.6 | 16 |

The four lines of *Orange* variety selected in 1937 on account of their low cyanide content were nearly as low in cyanide in 1938. We can speak of them as stable varieties, as regards this particular. That a low cyanide content is a stable character has been reported by Charlton (9) in Burma Beans (*Phaseolus lunatus*) selected for low content of hydrocyanic acid.

The reasons for ascribing stability to this character receive added strength from the fact that the conditions of growing in 1938 were most favourable for the accumulation of HCN in the plants, since drought prevailed throughout the vegetation period. And in spite of this the plants refused to increase in cyanide, compared to the content of 1937.

Not all of the varieties tested behaved however so as did *Orange 326*. The lines from the group *Gaolan* which had a reduced content of HCN in 1937 showed highly variable figures in 1938.

Table 5

Variation of HCN Content in Leaves of Certain Lines from *Gaolan* Group of Varieties

| Variety | Line No. | Percentage of HCN in raw weight of leaves | | | | Number of specimens tested in 1938 |
|---|---|---|---|---|---|---|
| | | Strains from harvest 1937 | Harvest 1938 | | | |
| | | | Minimum | Maximum | Average | |
| *Gaolan*: | | | | | | |
| 514 | 20 | 17 | 8 | 34 | 15 | 10 |
| | 45 | 17 | 12 | 62 | 32 | 21 |
| 37/A | 35 | 17 | 6 | 62 | 35 | 24 |
| | 36 | 12 | 8 | 42 | 18 | 17 |

The data in Table 5 show that while some of the lines proved stable enough, the other increased in the acid nearly 3½ times. The latter are of course more responsive to the conditions of growing.

The phenomena here reported are of great importance and not until they are thoroughly studied can we succeed in breeding for cyanide low varieties of sorghum.

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*PHYSIOLOGY*

# ON THE GROWTH MECHANISM OF FURROWS AND CONVOLUTIONS OF THE CEREBRAL HEMISPHERES

By M. E. AFANASSIEV

*(Communicated by I. I. Schmalhausen, Member of the Academy, 23. VI. 1939)*

Many research workers of the XIX and XX centuries studied the problem of growth and origin of convolutions (gyri) and furrows (sulci). There is hardly a notable anatomist, neuropathologist or psychiatrist who has not given his attention to the mysterious phenomenon of the wrinkling and furrowing of the brain. The pattern of furrows and convolutions was the first to strike the observer. However, it has long been known that this pattern is of little use for the understanding of the gyri and sulci, their significance and genesis. The second thing which usually arrested attention was the arising of the sulci. The interpretations of this phenomenon are numerous; all of them are contradictory and scarcely one conforms with the real state of things.

Seitz ([9]) connected the formation of furrows with the presence of blood vessels supplying the cortex with blood. Wundt ([12]) refers the same phenomenon to irregular growth of different cerebral areas, some of them growing more rapidly, while others are lagging behind. Ranke ([7]) and Bilschowsky ([3]) ascribe the appearance of furrows to the action of some unknown «form-building factor», the existence of which they took for granted. Retzius ([8]) interpreted the phenomenon by the growth of convolutions from some hypothetical «nipples» in the embryonic cortex. Monakov ([6]) considered (a priori) that furrows are formed from primal recesses, while convolutions arise at the expense of the rarefaction of furrows.

Schnopfhangen ([11]) suggested to explain this phenomenon by the influence of the adjacent conducting fibrils. Shaper ([10]) as well as Schaffer ([9a]) considers the appearance of furrows to be a secondary formation, resulting from alterations taking place within underlying strata of the cortex (lamina corticalis).

A number of authors working in this field of cerebral anatomy, abstain altogether from advancing their opinion [Landau ([5]) and many others].

With regard to the mechanism of growth of furrows there is no such confusion of opinion as about their origin. There are two principal theories. The first one, advanced by Seitz, takes the furrows to arise within the thick of the cortex and to grow through its upper layers. This opinion is seconded by Schaffer and Landau ([5]).

The second theory states that the furrows develop by means of invagination of the cortex layers. This opinion formulated by Jakob ([13]) was upheld by most of the authorities of the last century: Dareste ([4]), Baillarger ([2]), Ariens-Kappers ([1]), Monakov ([6]).

All the views and judgments cited above were based upon rough morphological observations or on histological studies of autopsy material. In the present work an attempt is made to disclose the mechanism of growth of the furrows without solving the question as to their origin.

The mechanism of the growth of furrows shows how this growth is realized, gives an idea of how the surface of the cortex is altered in the course of ontogenesis.

Unlike the work of all the authors listed above, the present work was conducted on living material with the application of the experimental method and subsequent verification of the results obtained under the microscope.

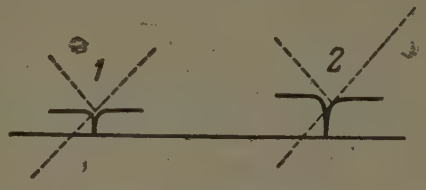


Fig. 1 shows the determination of the angulus.

At the moment of operation. 2 months after the operation.

M e t h o d s. The work was conducted on puppies (1—2 weeks of age). Finely ground sterilized charcoal was introduced under the first layer of the cortex into the angulus between a furrow and a convolution (Fig. 1). The operations were made under sterile conditions with the minimum possible traumatization. Charcoal did not provoke tissue degeneration. It was introduced by means of a thin injection needle to a definite depth determined in advance. The puppy was left to grow up, and was sacrificed 2 months later. Its brain was cut into sections on the microtome and subjected to histological treatment. This was followed by microscopical examination of the brain. The furrows induced with charcoal were compared with the normal ones. The angulus was determined by the perpendicular to the tangent drawn at the border between the sulcus and the gyrus.

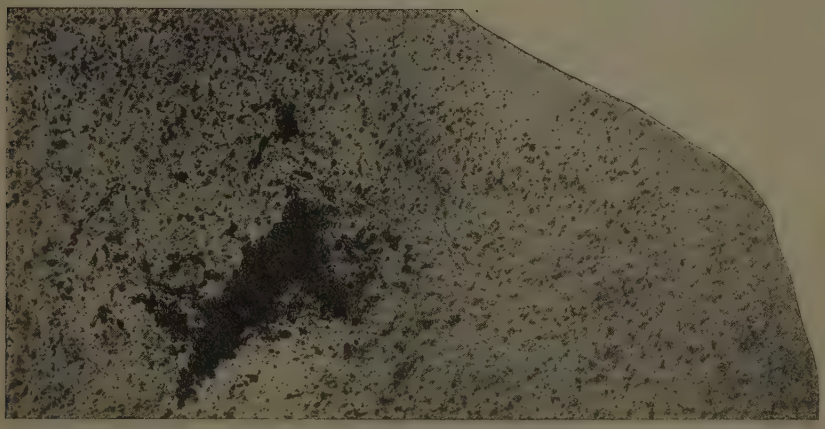

Fig. 2. The trace of the needle has remained on the angulus. Charcoal is visible in the shape of a black mass. Above—gyrus, on the left—sulcus. Section of the brain of a 2.5 month old puppy. Stained according to Niessl. The furrow is sulcus cruciata.

R e s u l t s. A comparison of the sulcus whose angulus was induced with charcoal with normal sulci showed no difference whatsoever. A tiny scar, or, to be more precise, a trace was visible in the sulcus which had been subjected to the experiment. This scar did not penetrate deeper than the first cortex

layer. Further than this there were no traces of the surgical intervention (Fig. 2). There was no trauma. The charcoal lay close to the scar, both of them being situated in the vicinity of the angulus. This should be taken to mean that during the two months that had passed since the operation, no displacement of the charcoal from the angulus had taken place. During this interval of time, i. e. a total of 2.5 months after the birth of the puppy, the furrow increased in depth from 2 mm at the date of the operation to 5.5 by the time of death.

The obtained results show the following:

1. Charcoal placed on the angulus of a furrow retains its initial position in spite of the growth of the furrow.

2. Since the furrow has grown during the 2.5 months of the experiment, while the charcoal has not been displaced, the layers of the surrounding cortex, i. e. the 1st and the 2nd layers, are not subjected to invagination.

3. No invagination of furrow takes place in the course of the postnatal period.

4. Wund's conception of the growth of convolutions seems to be the nearest to the actual state of things.

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*HISTOLOGY*

# ON THE RÔLE PLAYED BY THE SO-CALLED DARK CELLS

By G. YASVOIN

*(Communicated by I. I. Schmalhausen, Member of the Academy, 26. VI. 1939)*

Dark cells, differing from the usual light cells by their smaller size, angular shape and intense diffuse staining of both protoplasm and nucleus, have been studied in greatest detail in the liver. Some authors regard them as degenerating elements, while others think them capable of transforming in some cases into the usual light cells, others again consider them to be special «choleopoietic» elements. At the same time there are indications that the dark cells of the liver are mere artefacts. Yet, most authors do not take into consideration the circumstance that dark cells are encountered not only in the liver, but have been described also in other organs and tissues (thyroid gland, intermediate lobe of the hypophysis, chondro- and osteoblastic tissues, the central nervous system and ganglia, in cancer of the mammal gland*), and that the question regarding the rôle of the dark cells in the liver is only a part of a more general problem.

I had observed dark cells in the odonto- and osteoblastic tissues ([1–4]), as well as in loose connective tissue ([5]) and in the epithelium of the enamel ([6]) and of the crystalline lens ([7]). At present I have supplemented these observations by a study of the dark cells in the liver, pancrease and intermediate lobe of the hypophysis, in the epithelium of the cornea, skin and of some mucous membranes, in the follicular epithelium of the ovarium, in both sheets of the eye-cup, in the ganglia (spinal and sympathetic) and in the developing neurospongium.

In each of these organs or tissues I was able to state the presence of typical dark cells, and the features and relations characterizing them appear perfectly similar in each case. This alone shows that the dark cells are not such elements which accomplish some function specific for this or other organ or tissue, but that their inherent properties are the expression of a certain condition, which may be assumed by the cells of different tissues or organs. My data concerning the alterations and transformations of dark cells testify to that this condition is an intravital one and that the dark cells in fixed preparations are its «equivalent picture». At the same time I became convinced that dark cells may appear in preparations also as the result of injury suffered by the tissue during fixation, i. e. as an artefact. However, this circumstance does not commit those dark cells which have arisen and exist intravitally, independent

* The opinions expressed concerning the rôle of dark cells in these organs and tissues are also greatly contradictory.

of any artificial influence. The possibility of an eventual artificial production of dark cells as a result of tissue injury during fixation merely points to that the intravital transformation of the common cells into dark ones (resp. their passing into a condition, in which they appear dark in fixed preparations) is determined by some kind of depression of their life activity, since in both cases similar morphological alterations set in.

And indeed, the life cycle of the dark cells, at least in those objects in which I and some other authors ([8,9]) succeeded in tracing it, can be divided into two periods. The first period is characterized by the loss of normal turgor, connected with a decrease of the water content of the cells and gelatinization of their protoplasm. Such a condition of the cells, as it has been established by me in a number of earlier works ([1-7]), is reversible up to a certain moment. It seems to correspond to that intravital condition which has been designated as paranecrotic by Nassonov and Alexandrov ([10]). In some cases the dark cells come out of this paranecrotic condition and are transformed into lighter staining, higher differentiated ones and finally into light, definitely differentiated cells. In other cases the phenomena which characterize the first paranecrotic period continue progressing, and the dark cells enter their second period, during which they degenerate and finally disappear as such. This degeneration is, however, expressed not in a disintegration of the dark cells, but in their total ectoplasmatic transformation. As the result of this peculiar (plastic) degeneration, there arise metaplasmatic (resp. intercellular) formations, the character of which is determined by the tissue, to which the dark cells in question belong. Thus, the plastic degeneration of connective tissue dark cells ends in their total transformation into argyrophile fibrils which later are transformed into fibrils of the basic sustance. In the nervous tissue the plastic degeneration of the dark cells leads to their total transformation into fibrils of the gliae (or in the exterior sheet of the eye-cup into neurokeratinic substance). Epithelial cells are transformed as a result of plastic degeneration into a cell-cementing substance or into corresponding delimiting envelopes. Thus, the dark cells perform, but in a particularly high measure, the same plastic function as is generally accomplished by the cells of the tissue they belong to. As I have established, the participation of the cells in the production of metaplasm assumes new forms and is reduced or even entirely stopped with their progressing differentiation and transformation into light cells. Only little differentiated cells or, more precisely, those which after their mitosis just begin to differentiate, turn dark and participate actively in the production of metaplasm until their plastic degeneration*. The cells may become more or less dark (on their way to the transformation into light cells) also during the next stage of their differentiation, following the initial one, and the duration of this second stage, in which the cells show as yet some capacity towards mitosis, seems to vary according to the tissue.

These regularities proper to the dark cells become particularly demonstrative when studying the development of such organs, as the tooth and the eye whose cellular elements are regularly oriented and differentiate in a definite sequence. It has been pointed out that the development of the cells of nervous tissue remind one of the development of spermatozoids. A still fuller analogy, though not a complete one either, I see in the processes of differentiation of the cells of nervous and connective tissues. And indeed, during the development of, say, the osteo-or odontoblastema the mesenchymatous elements divide and after division are transformed into dark cells—pre-osteoblasts or pre-odontoblasts—and later into light, highly differentiated osteo-

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* The condition of paranecrosis may, possibly, not only testify to, but also determine the beginning of the differentiation of these cells.

and odontocytes. At the cost of the former radial fibrils are formed, at that of the latter the tangential fibrils of the bone and dentine. During the development of the neurocytoblasteme—the tissue of the nervous tube (resp. of the retina)—the cells divide and are transformed into dark cells—the proneurocytoblasts, some of which produce the radial fibrils of the glia (in the retina—Müller's fibrils), while others turn into more lightly staining neurocytoblasts, forming the neurospongium. Later part of the neurocytoblasts is transformed into light cells, neurocytes (neurons), others remain as astroblasts which, possibly, still later differentiate into astrocytes.

In this connexion it should be noted that both the mesenchyme and the tissue of the nervous tube (evidently the ecto- ento- and mesoderma, too) are initially ectoplasmatic syncytia. With their progressing differentiation the ectoplasm, into which the nucleo-endoplasmatic areas of some of the cells of the syncytium may totally transform, is totally or partly transformed into the intracellular substance of some or other tissue. In connexion with this the nucleo-endoplasmatic areas of the syncytium become individualized cells, connected (or separated) not by cellular ectoplasm, but by entoplasmatic intracellular substance: in connective tissue—by basic substance, in nervous tissue—by glia, in epithelium—by cell-cementing substance.

These regularities of differentiation are distinctly expressed not only in the embryo, in developing bone, dentine, retina, nervous tube, enamel or crystalline lens, but in the adult organism, too—in follicular and many-layered flat epithelium. The idea of the rôle played by the dark cells and of the process of differentiation I have formed on the ground of my studies on the objects enumerated above is corroborated by the data, which I was able to establish for the liver, pancrease and hypophysis. Each of these organs contains elements capable of division which, the mitosis ended, become dark cells. Having entered the process of differentiation, one of the expressions and results of which is the formation by the dark cells of ectoplastic envelopes (walls of biliary ducts, membranes separating the cells from the blood vessels and from one another, closing platelets), part of these dark cells suffer total ectoplastic transformation, others are gradually transformed into more lightly staining and, later on, into light, highly differentiated cells. The intermediate (lighter staining) forms preserve the capacity to mitosis.

The dark cells, encountered in certain numbers in ganglia, uninjured during fixation, seem also to be such intermediate forms, i. e. not definited differentiated elements*.

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* Schreiber und Wengler ([11]) have experimentally shown even «adult» ganglial cells to be capable of mitotic division.

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*PLANT PHYSIOLOGY*

# SOME RESULTS OBTAINED IN CHANGING THE NATURE OF PLANTS BY MEANS OF GRAFTING

By G. KH. MOLOTKOVSKY

*(Communicated by A. A. Richter, Member of the Academy, 4. VI. 1939)*

Facts of explicite mutual influence between the stock and the scion have now abundantly accumulated in horticultural practice.

The works of many investigators have shown the possibility to produce hybrids by means of grafting.

The concepts of Darwin, Michurin and Lyssenko have made the basis of some experiments of preliminary nature carried on at Zhitomir Agricultural Institute in the years 1937 and 1938. The results obtained are briefly summarized here. The plants involved in the experiment were several varieties of potato, Jerusalem artichoke, dahlia, tomato, hop, hemp, wheat and barley.

I. Experiment with Potato. The 17 varieties of potato used in the experiment varied with regard to the length of vegetation period, starch content, colour of tubers and other characters. More or less pronounced influence of the scion upon the stock and conversely was observed in most of the graftings. The changes involved the habitus of the shrub, of leaves, particularly the colour of tubers and the length of the vegetation period.

The method employed in growing the grafts was chiefly that suggested by Lyssenko: the scion was deprived of leaves partly or entirely and thus forced to take his food from the assimilates of the stock. The reverse was the case when the object was to increase the supply to the scion at the expense of the stock.

The following is an account of mainly morphological modifications observed after grafting some potato varieties.

A) «White Horn» upon «Grace». The tubers of the stock changed in form and colour. Instead of red tubers peculiar to «Grace» the plants produced white tubers which by their form often suggested a horn. Under some of the bushes both red and white tubers were found. With regard to the structure of leaves the scion looked intermediate compared to controls «White Horn» and «Grace». Ripening set in 15—20 days earlier than in «Grace».

B) «Woltman» upon «Industry». The tubers of the stock were pink, pale-pink; occasionally white, not peeling as were the controls of «Industry» and 1.5—2 times greater in size. The bush was higher, and the tubers were set closer together.

C) «Woltman» upon «Early Rose». Most of the tubers were pink, but some were red or white. The scion from «Woltman» produced coarse shortened leaves with strongly developed vein system. The vegetation period was 35 days longer compared to control «Early Rose».

D) «Princess Negra» upon «Bovinia». The tubers varied in form from round to elliptical and were partly coloured from white-red and red-bluish to bluish («Princess Negra» has bluish tubers with round spots). The bushes were stunted with thick stems and coarse leaves.

E) «Great Scott» upon «Ever Good». Oblong and round tubers with white flesh as in «Great Scott». The controls of both varieties flowered sparsely. The bush reached a meter in height.

F) «Lorch» upon «Heimat». The bushes made vigorous growth and reached a height of 1200 cm. They were very floriferous and one of them set two berries, while no berries is ever produced by «Lorch». The tubers were white, oblong, somewhat flattened at one of the ends. The vegetation period was 15 days longer compared to control «Heimat».

G) «Fir Cone» upon «Palchiki». The graft ripened 10 days earlier than did the control «Palchiki». Tubers white, oblong, slightly curved. Their eyes had sharply expressed brows jutting out 1—1.5 mm. From this fact arose their resemblance to fir cones. The bushes were considerably higher compared to «Fir Cone» controls.

II. Experiment with Various Plants. A) Jerusalem Artichoke. Two varieties were involved in the experiment: «Maslovskaya Krasnaya» with red tubers and round leaves. Stem height about 2—3 m. Under conditions prevailing at Zhitomir its time of flowering is the middle of October. Accordingly, no seeds are usually set, because the inflorescences are in most of the cases injured by the frost. The other variety was a decorative plant with red small tubers, small almost cordate leaves on short petioles. Stem sparingly covered with leaves, about 1—1.5 m high. Flowering sets in towards the end of August. This variety was grafted upon by «Maslovskaya Krasnaya». The graft took well.

The scions developed more energetically compared to the controls of decorative variety. They formed stronger leaves and stems approaching in these particulars to «Maslovskaya Krasnaya». Flowering started September 12—14, i. e. 18—20 days later compared to the controls of decorative variety, but more than one month earlier compared to the controls of «Maslovskaya Krasnaya». The plants came into seed. Externally there was no difference in the tubers between the experimentals and the controls. It will be obvious that here the influence of the stock upon the scion was to accelerate its entering into the reproductive phase.

It is a matter for regret that no reverse grafting, i. e. of the decorative form upon «Maslovskaya Krasnaya», was explored.

B) Hemp upon Hop. The hop raised in pots was grafted upon by Italian hemp. Grafting was affected as follows. Throughout the length of a meter from the base of the stem small longitudinal slits were made at 15—20 cm intervals. They had to take hemp stems sharpened at the base and as long as to bear 4—6 leaves, of which all but one or two were removed. The scions were fastened with raffia.

The grafts took better at the base of the stem, but the total of the scions survived was very low. Out of 47 plants grafted only three came to flower. Most of the others died during their second month on the stock. Those which survived attained a height of 25—30 cm. The three specimens mentioned produced only two hemp seeds which would look like a normal hemp seed but for their size. They were 0.5—1 mm across.

The few attempts to raise the hop on the hemp were a failure.

C) Potato with Tomato. Potato variety «Ella» was grafted upon by tomato variety «Chudo Rynka» and conversely. In two sets the stocks were deprived of their leaves to make them take up the assimilates from the scion. There was also a set, in which the tomato scions grown upon

a potato root were deprived of their leaves after flowering. Accordingly, their fruits may be said to have developed at the expense of the assimilates from the stock, if we neglect the assimilating power of the green stem of the scion. The result was that the fruits on the scion developed slowly and were 2—3 times smaller than in the control. But the flesh of the fruit had a more agreeable flavour (was more friable), the seeds were larger and their number was 1.5—2 times that in the control tubers of equal size.

When variety «Ella» was grafted upon the tomato variety mentioned it produced strongly ruffled leaves. This phenomenon, however, showed a tendency to decrease or even vanish entirely in those specimens, in which the scion was a cutting taken from a sprout which had freshly emerged from a tuber. If the cutting of potato was taken from an adult plant, it often produced aerial tubers at the base of those leaf-stalks which were near to the site of union.

This goes once more to confirm the statement of Lyssenko's theory that the whole plant is not equivalent from the standpoint of phasic development. This statement is not to be disregarded when we have to select the cuttings, especially for the purpose of interspecific or intergeneric vegetative union.

D) Cereals. In passing the possibility of cereal grafting was explored. The test was run with two barley varieties Colchicum 10/30 and Verkhniachsky 06 and a wheat variety Garnovka Kochina.

The barleys were grafted upon each other and the wheat was grafted upon the variety Colchicum 10/30. The inarching method was resorted to. The varieties were grown separately in boxes. Then each pair to be grafted was pricked off in a pot, where the plants were joined by approach. 10—12 days later after the tissues had grown together, the seedling which had to be the scion was cut a little underneath and its leaves were partly removed. The wound thus occasioned was smeared over with garden paste. After 4—5 days more the scion was cut off entirely. Grafting was made in a greenhouse. The technique of moisting chambers was not applied. After being kept for 3—4 days in the shade, the pots with grafted symbions were placed out-of-doors.

The plants showed a very low viability. Out of 78 grafted specimens only five produced flowers: Colchicum 10/30×Verkhniachsky 06—2 specimens; Verknniachsky 06×Colchicum 10/30—3 specimens. But even these failed to set seeds.

The interesting fact to note here is that wheat variety Garnovka Kochina was living upon the barley Verkhniachsky 06 for a rather long time and only just before flowering did it succumb.

E) Jerusalem Artichoke, Dahlia and Potato. The results were invariably negative, whether the Jerusalem artichoke was grafted upon the dahlia or vice versa, and grafting the dahlia upon the potato, variety «Woltman», and conversely was a failure too. It is worth mentioning, however, that the Jerusalem artichoke held up on the dahlia for nearly 1.5 month, and even produced new leaflets, but finished with dying. In most of the cases the process of dying off started at the base of the scion, at the place of its union with the stock. Less frequently we observed the stock to begin withering and dying at the place of union.

Potato cuttings held also well upon dahlia. They died after 15—20 days on stock and sometimes later. Contrary to this, the dahlia cuttings on potato perished very soon.

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*PLANT PHYSIOLOGY*

# CHEMICAL TREATMENT OF WINTER WHEAT SEED AS A MEASURE TO INCREASE FROST RESISTANCE

By A. VETUKHOVA

*(Communicated by N. I. Vavilov, Member of the Academy, 4. VI. 1939)*

Evidence furnished by the author's previous investigations is that a change in the frost resistance of winter cereals is concomitant to sharp qualitative and quantitative changes in the condition of their colloids, whereby the hydrophylity of the latter is one of the basic indices for tolerance of plants to low temperature (1). This result suggested that the frost resistance of winter cereals might possibly be increased by such physiological methods which would make the colloids more stable. To explore this possibility was the aim of the present investigation.

In the past a number of works were devoted to the study of protective substances in connexion with the frost resistance of plants. Lidfors(2) explained the protective action of sugars against low temperature in terms of their ability to prevent proteins from coagulation. N. A. Maximov (3) established the protective action of salts against freezing on leaf cuts and postulated its relation to the eutectic point of the substance. The reason for increased stability of the tissue seems essentially to lie in the stabilizing action of the ion upon the colloid micella; the latter undergoes a change in its charge value and hydrogenation. The stabilization of colloidal systems can be effected with the aid of physical and chemical factors, which have to come into play at that stage of development when the plant actively responds to external influence.

The stabilizing substances can be applied in various ways: through the root system by means of a suitable combination of fertilizers, through the leaf surface by spraying, and lastly by means of pre-sowing treatment of the seed. A judicious combination of agrotechnical methods is also a means to increase the stability of colloids.

The present paper deals with only one item, the influence of the pre-sowing chemical treatment of seeds on the frost resistance of winter wheat. This method is considered by us as most simple and adaptable in practice.

Preliminary tests for the action of various chemical substances on the resistance of colloids were run with colloid solutions obtained from the leaves of winter wheat. A solution of the chemical substance concerned was added (1 $cm^3$) to the colloid solution (5 $cm^3$) and the absence or the extent of coagulate formation was the measure to estimate the stabilizing or the coagulating effect produced. The same colloidal solution without the chemical substance served as control. In some of the experiments freezing of the colloidal solution added with the chemical substance concerned was carried out.

The investigation involved the effect of varying anions with a constant cation (KSCN, KI, KCl, $K_2SO_4$) and the effect of varying cations with a constant anion (KCl, NaCl, $CaCl_2$, $BaCl_2$), as well as the action of hydroxides of alkali metals and of alkaline earth metals [NaOH, KOH, $(BaOH)_2$ $Ca(OH)_2$] and some phosphates. The concentrations of the solutions were $n/10$, $n/100$ and $n/1000$. The anions were found to be decreasingly protective in the order: KSCN>KI>$K_2SO_4$. The latter was responsible for a certain coagulation. The regularity in the influence of anions fits in with Hofmeister's series for alkaline and neutral protein.

In the experiment on varying cations a protective action was shown by weak solutions ($n/100$ and $n/1000$) of Na and K chlorites, whereby the action of K was less strong. No protective action was produced by Ca and Ba salts, and if their concentration was $n/10$ or higher they even favoured coagulation. The coagulating action was weaker in the case of Ba than in the case of Ca. The fact that Na and Ba are more hydrophilous may, possibly, explain their higher protective action compared to K and Ca respectively.

The tested hydroxides of the alkaline and the alkaline earth metals [NaOH, KOH, $Ca(OH)_2$, $Ba(OH)_2$] were found to increase the stability of colloids, the former being thereby more active than the latter. The tribasic potassium salt of phosphoric acid was also protective against coagulation, while the monobasic salt was not, and this is evidence of the reaction being a very important factor in the change of the stability of colloids. The results obtained by these preliminary experiments have made the basis for studying the frost resistance of germinated seed under the action of various chemical substances.

According to literary data, the properties of the plant, its development and yield can be changed by pre-sowing treatment of the seed after dormancy has been broken. The possibility to induce such changes in plants has been demonstrated by Lyssenko (4) and his associates. Vorobiev, Genkel and Kolotova were able to increase the resistance of plants to drought by heating the seeds before sowing (5) and alternately soaking and drying them (6). In a paper by Briguinetz(7) it has been reported that the node of tillering can be deepened by treating the seeds with light. Still other reports have been made along this line of investigations which are not referred to here on account of the space available. Our choice of chemical substances whose action on the frost resistance of germinated seeds and adult plants we had to study was directed by the wish to meet the following requirements: permeability of the cell by the substance concerned; no detrimental influence of the latter on the viability of the cell and the presence of a stabilizing influence.

In testing the frost resistance of emerged sprouts under the action of chemical substances we soaked the seeds of two winter wheats (No. 1239 and Kooperatorka) in chemical solutions until scarcely visible germination set in (the amount of solution was 30% of grain weight). Then they were subjected to low temperature, —4°C (in some of the experiments, —7°C) for 24 hours. The percentage of survival was the value for estimating the relative frost resistance. The tests involved the chlorates and the citrates of alkali metals (Li, Na, K) and hydroxides of alkali metals and alkaline earth metals (Na, K, Ca, Ba).

If the concentrations were $n/100$, $n/1000$ and $n/10000$, the effect of salts and hydroxides of alkali metals was to increase frost resistance in the emerged seedlings. It the concentration was $n/10$, most of the substances affected the germinating power unfavourably. Some of them did so even with a $n/100$ concentration ($Li_3C_6$ $H_5O_7$, KSCN). These are of poisonous nature to the plant. Accordingly, the seeds treated with such solutions showed reduced frost resistance.

The hydroxides of alkaline earth metals had a much weaker effect. This was probably because their power of penetration was less, while the cation interfered with stabilization of colloids.

The next step was to try the pre-sowing chemical treatment of grains during hibernation. The experiment was arranged with two winter wheats (No. 1239 and Kooperatorka) in the experimental field of this Institute (near Kharkov).

Dry and water soaked seeds served as control. Planting was done in 1.5 m plots, in 5 sets under wooden planks. During winter the plants were periodically dug up and tried for relative frost resistance by means of direct freezing in a refrigerator. The value to compare their frost resistance was the percentage of plants which survived freezing. In order to characterize the stability of colloidal system there was moreover a test for hydrophility of colloids. Determination was made in the leaves of winter wheat with a refractometer.

The substances whose action was studied were salts and hydroxides of alkali metals (Li, Na and K), the monosubstituted and the trisubstituted phosphate of potassium. The results are summarized in Table 1.

Table 1

Frost Resistance of Winter Wheat During Hibernation as Affected by Pre-Sowing Chemical Treatment of Seed

(% of survived plants)

| Date of sampling and temperature of freezing | No. 1239 | | | | Kooperatorka | | | |
|---|---|---|---|---|---|---|---|---|
| | 30.X −10° | 9.XII −12° | 28.XII −15° | 27.III −9° | 30.X −10° | 9.XII −12° | 28.XII −15° | 27.III −9° |
| Control (dry seed) | 51 | 48 | 45 | 91 | 20 | 48 | 58 | 58 |
| Control (water soaked seed) | 51 | 47 | 57 | 93 | 24 | 41 | 48 | 64 |
| NaCl *n*/100 | 70 | 73 | 78 | 95 | 50 | 76 | 67 | 82 |
| » *n*/1000 | 78 | 63 | 80 | 100 | 55 | 74 | 62 | 68 |
| $Na_3C_6H_5O_7$ *n*/100 | 63 | 69 | 81 | 94 | 62 | 58 | 74 | 62 |
| » *n*/1000 | 76 | 58 | 73 | 94 | 64 | 58 | 62 | 68 |
| NaOH *n*/100 | 70 | 72 | 74 | 96 | 53 | 77 | 60 | 77 |
| » *n*/1000 | 72 | 73 | 57 | — | 58 | 58 | 70 | 79 |

From these data it is obvious that the effect of the salts and hydroxides of alkali metals in *n*/100 and *n*/1000 concentrations (in the table only the data for Na are referred to) is to increase the frost resistance of plants under natural conditions of hibernation. The same is true of the action of the trisubstituted phosphate of potassium (two estimations were made during winter).

The stability of the colloidal system was also strongly affected by the chemical treatment of the seeds, as is shown in Table 2.

Those substances and concentrations which have increased the hydrophility of the colloids have also increased the frost resistance.

The conclusion to be drawn from the results obtained is that the presowing treatment of the seeds with chemical substances greatly affects the qualities of the adult plant as it increases its resistance to low temperature.

The relative frost resistance could not be established properly by inspecting the plants in spring, because the ratio of winter killed plants was quite insignificant even among the non-resistant Kooperatorka.

Table 2

Hydrophility of Winter Wheat During Hibernation as Influenced by Chemical Treatment of Seed

| | Grams of water bound by one gram of substance | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | No. 1239 | | | | | Kooperatorka | | | | |
| | 29.X | 10.XI | 20.XI | 27.XII | 19.IV | 29.X | 10.XI | 20.XI | 27.XII | 19.IX |
| Control (dry seed) | 0.172 | — | — | — | Absolute values of bound water quite insignificant | 0.126 | — | — | — | Absolute values of bound water quite insignificant |
| Control (water) . . | 0.174 | 1.177 | 0.187 | 0.179 | | 0.132 | 0.132 | 0.171 | 0.177 | |
| NaCl $n/100$ . . . | — | 0.217 | — | — | | — | — | — | — | |
| » $n/1000$ . . . | 0.215 | — | 0.232 | 0.230 | | 0.233 | — | — | 0.231 | |
| $Na_3C_6H_5E_7$ $n/100$ | — | — | — | — | | 0.198 | 0.199 | — | — | |
| » $n/1000$ | 0.218 | — | — | 0.195 | | — | — | — | — | |
| NaOH $n/100$ . . . | — | 0.217 | — | 0.205 | | — | 0.209 | — | 0.203 | |
| » $n/1000$ . . | 0.230 | — | 0.244 | — | | 0.203 | — | 0.210 | — | |

At present both the theoretical and practical aspects of the subject are being more thoroughly investigated at this Insitute. There are grounds to suppose that the method of stabilizing the colloids may be turned to account for increasing the drought resistance of plants.

Experiments of preliminary nature have been started along this line and they show that the winter wheat seedlings increase their resistance to high temperature (+48, +52°C) in response to the treatment of their seed with salt solutions of certain alkali metals.

Ukrainian Institute of Socialist Agriculture.
Kharkov.

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*ANIMAL PHYSIOLOGY*

# EFFECT OF VITAMIN D ON THE GROWTH AND PROPAGATION OF *GAMBUSIA* AFF. *HOLBROOKII*

By G. V. SAMOKHVALOVA

*(Communicated by I. I. Schmalhausen, Member of the Academy, 14. VI. 1939)*

Gambusia is a small viviparous fish of the family *Poeciliidae*, which owing to its ability of destroying moskito-larvae and its modest requirements is being successfully applied in combating malaria. The gambusia imported into this country from Italy has become well acclimatized in the Caucasus, in the south of Ukraine and in some regions of Middle Asia. At the present the task is set to extend the range of gambusia to more northerly latitude of the Soviet Union.

| Date of birth | Age | Sex | Quantity | Length in mm | Average weight in mg |
|---|---|---|---|---|---|
| 1934 | 3 years | ♀♀ | 50 | 25—30 | 201 |
| | | ♂♂ | 2 | 26—27 | 120 |
| 1935 | 2 » | ♀♀ | 44 | 26—30 | 215 |
| 1935 | 2 « | ♂♂ | 19 | 23—25 | 143 |
| 1937 | 10 months | ♀♀ | 31 | 27—30 | 205 |
| 1937 | — | ♂♂ | 30 | 25—28 | 152 |

While studying the biology of gambusia, we became aware of underdevelopment in male and chiefly female gambusia reared in laboratory aquaria as compared to their satisfactory growth in natural waters of our region. The table presents data on the size and weight of gambusia bred under ordinary aquarium conditions. Gambusia females from natural waters of Caucasus or of our region have an average weight of 600—1000 mg and more, whereas the males weigh about 200—250 mg. The comparison of these figures to those shown in the table are illustrative of the underdevelopment of gambusia reared under ordinary aquarium conditions. The males of gambusia are 25% short of their normal weight, whereas the females weigh 3—4 times less than normal ones. The reproductivity of these aquarium-reared females likewise proved to be strongly reduced.

The fact that gambusia reared under aquarium conditions proved underdeveloped made it necessary to study the causes underlying this phenomenon.

Special experiments on the effect of volume, density of population and temperature of the aquarium upon the growth of the aquarium-gambusia have shown these factors, though affecting the growth, as of any other fish, to be of minor importance to account for its underdevelopment under aquarium conditions. The growth and development of gambusia in laboratory aquaria, even under optimal conditions with regard to the above factors, proceed at a much slower rate as compared to their rapid growth in natural waters.

In the summer of 1936 we have placed young and adult gambusia (a total of about 100 individuals) into the basin of the glasshouse of the Botanical Garden. No serious progress as regards increase in growth and reproductive capacity of gambusia was recorded from these basins.

In 1938 we have undertaken special experiments on the study of the effect of sunlight on the growth and propagation of gambusia. For that purpose several aquaria with gambusia were kept during the summer on an open platform on the roof of the Botanical Institute. The aquaria were half covered with glass, so that the gambusia was exposed to the benefit of direct sun rays. The fish remained on the roof from June to the end of September, after which it was transferred to the Laboratory. The results of this experiment are summarized in Fig. 1.

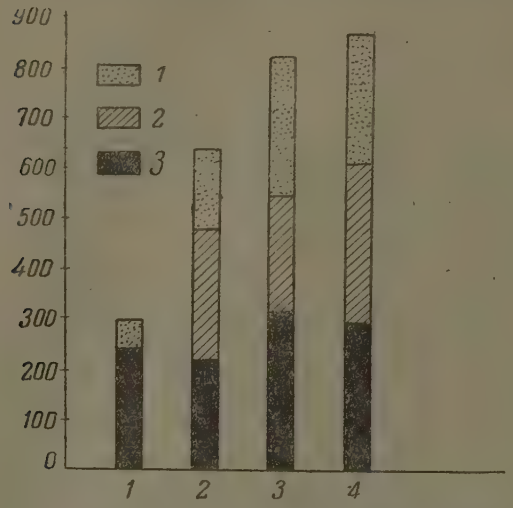


Fig 1. Increment in underdeveloped gambusia under the action of sunlight: *1*—control group, *2*, *3* and *4*—experimental groups.

The first group of females—the controls — stayed during the entire period in the laboratory aquaria, while the 2nd group of females was taken for experimental observation when 1 year old, and the 3rd and 4th at the age of 6 months. Fig. 1 shows the experimental gambusia to attain a far greater weight than the control one, namely 650 mg the second group, and 870 mg the 3rd and 4th groups of females kept on the roof and in the laboratory. In this connexion it should be noted that the gambusia continued to grow not only during the summer, but throughout the winter period as well, after it had been transferred into laboratory conditions, whereas the group of female controls has shown a small rate of increment (about 20%) for the entire duration of the experiment. The females of the control group began to multiply and produced normal young.

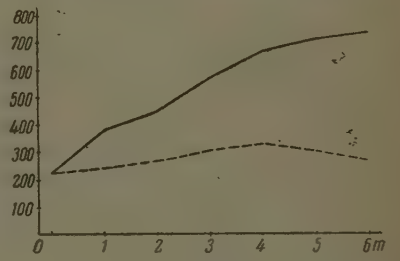


Fig 2. Growth compensation in mature females of gambusia treated with vitamin D. Upper curve — experiment, lower— control.

The above experiment, as well as a number of others, suggested the idea that sunlight is one of the basic factors determining normal growth and propagation of gambusia both under natural and aquarium conditions.

The fact that gambusia transferred from field conditions and aquaria, where they have enjoyed sunlight, into laboratory quarters continue for some time to grow and reproduce, points to that when exposed to sunlight they store up a certain amount of energy expressed in terms of vitamin sub-

stances. It is known that under the action of the ultraviolet part of the sun spectrum, vitamin D is being produced in the animal organism.

To find out why sunshine exerts a favourable effect upon gambusia, we have performed special experiments on supplementing the diet of the aquarium gambusia with that vitamin. A vitamin D-preparation has been added by us to dry daphne in the amount of about 6 drops to 4.5 g of daphne. Daphne + +vitamin D were mixed and administered daily to the fish under experiment. On the average each fish was fed one vitamin unit per day.

We have arranged 2 series of experiments: under the first series was studied the curative effect of vitamin D upon the growth of the underdeveloped aquarium-gambusia (60 ♀♀), under the second—the prophylactic influence of vitamin D on the growth of gambusia under aquarium conditions (120 young specimens). The experiments have proved that gambusia of the first as well as of the second series does not only show better growth as compared to the control group, but begin to reproduce bringing forth normal offspring.

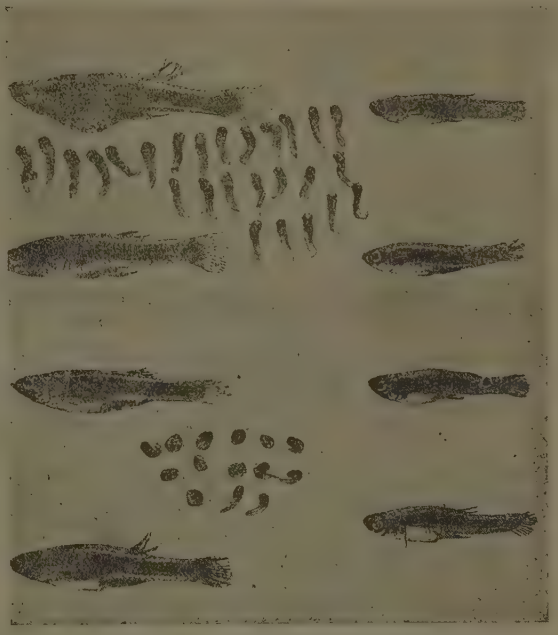

Fig. 3. Photograph of gambusia females from experiment 2 of the first series. Left—females under experiment, right—controls.

Fig. 2 illustrates the growth of 10 experimental and 10 control females of gambusia from experiment 1, under observation for a period of 6 months. The curves indicate that the tested females attained during that period on the average 750 mg in weight, while the control ones showed practically no increment. Two months after the beginning of the test sex-mature males were placed among the females for mating. The experimental females began to spawn and produced quite satisfactory young, while among the controls none was found to be pregnant.

Fig. 3 presents photographs of female gambusia from experiment 2. Females from that group were fed vitamin D for a period of 5 months. 25 days after mating the females were autopsied and some of them photographed (Fig. 3). One of the experimental females produced 26 completely formed young and the other one—14 in a less advanced stage of development, whereas among the control females no cases of gestation were observed.

Fig. 4 summarizes the results of exp. 6 of the 2nd series on the growth of the young of gambusia under the action of vitamin D. Along the axis of abscissae is plotted the age in days, against the axis of ordinates—the length in mm. Experiments of the given series were conducted by us in such a way that half of the young of each spawn were used as controls. The controls

were fed dry daphne+olive oil, because vitamin D (in the commercial preparation) is furnished in olive oil. The volume of the aquarium, the temperature and density of population were identical both for the experimental and control group. The young of gambusia were regularly measured. From the results of the experiments it became eivdent that young fish fed vitamin D do not only grow more rapidly than the control ones, but attain sexual maturity much more rapidly, too. The sex of the young of the experimental group can be determined at the age of 1 to 2 months (Fig. 4), whereas in the control group sex determination is possible considerably later. Similar data were obtained by us from all the experiments of this series.

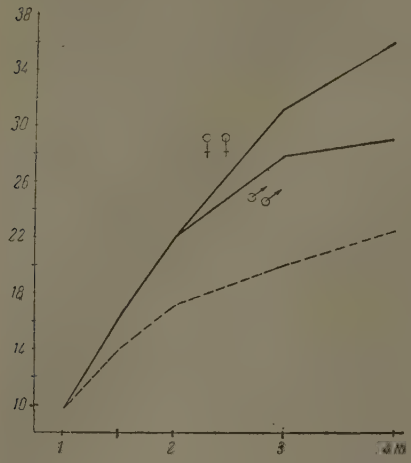


Fig. 4. Growth curves of the young of gambusia from experiment 6 of the 2nd series. Upper curve—experimental group, lower—control.

Thus, the experiments have proved that by supplementing the food of gambusia with vitamin D, growth, sexual maturity and propagation of gambusia are promoted. Females of gambusia underdeveloped as a result of breeding under aquarium conditions, upon receiving vitamin D in addition to their food exhibit so-called growth compensation and begin to reproduce. The young of gambusia fed vitamin D make better growth and attain sexual maturity at an earlier age.

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*EXPERIMENTAL ZOOLOGY*

# ON THE FACTORS OF ARTIFICIAL OSTEOGENESIS

By M. A. EGOROV

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At the present time it becomes possible to approach the analysis of processes occurring in the tissues after surgical grafts from the viewpoint of the problem of organizers. As a matter of fact the methods and material used by surgeons for tissue transplantations have very much in common with the «insertions» of N. V. Nassonov (1). For the purpose of compensating tissue defects or that of grafting some organ necessary for the patient, surgeons insert the respective tissues or organs (or parts of them) into the tissues of patients under conditions of auto- or homo- or heteroplastics. N. V. Nassonov in studying the form-building activity of organizers, inserted under the skin of axolotls bits of cartilage, muscle, bone, epithelium, lung, intestine, gill, liver, kidney, brain, heart, swimming bladder, sexual glands, urinary bladder, taken from axolotls, lizards and fishes. He found that the tissues thus inserted may become grafted in the organism of the host, but may also suffer disintegration. In the latter case form-building at the site of insertion is eventually observed, while in the former it is never the case. Form-building has been observed by Nassonov after insertion of cartilage, lung, liver, intestine or gills. The nature of the form-building process consists, according to Nassonov, in that the cells of the inserted material undergo histolysis and the products of this lysis act as «organizing substances»: some of them destroy the cutis, others stimulate the epithelial cells to proliferation, others again control all these processes.

For the viewing the processes which are observed in surgical grafts, under this aspect, I chose as test object the mucous membrane of the bladder of the dog which, as this is known from the studies of Leriche and Lucinesco(2), being inserted into the subcutaneous or intermuscular tissue of the same animal, induces inevitably the formation of osseous tissue at the periphery. Histologically the following is observed in these cases: the cells of the transplanted mucous membrane at first proliferate and form a nodule; a few days later the cells in the central part of the nodule are necrotized, and a cavity containing liquid is formed; by the 15—20th day the fibres of the surrounding connective tissue begin to resemble collagenous fibres; beginning with the 20—25th day, the transformation of the cells of the connective tissue into osteoblasts and the formation of osseuos tissue around them is noted.

I repeated the experiments of Leriche and Lucinesco on 4 dogs. A piece of the bladder was cut out from dogs subjected to a morphine-ether narcotiza-

tion, the wound of the bladder was closed by a double suture. The mucous membrane was separated with utmost caution from the bladder piece and small bits of this mucous membrane, averaging in size from 2×3 to 2×5 mm were inserted into subcutaneous pockets, which were made with nippers on both sides of the loparotomy wound. From the very first days we observed at the sites of insertion swellings, the size of a pea to that of cherry. Gradually these swellings became harder and somewhat decreased in size; by the end of the month they were felt as strictly limited tumors, hard as bone and of an irregular ball-like shape. These tumors were resected on the 30th and 45th days. Macroscopically the tumors were found to be cysts with osseous walls. The cavities of the cysts contained a viscous dark-brown liquid. Histological examination showed that the cavities of the cysts were paved on the interior side with epithelium of intermediate type, in some places many-storeyed,

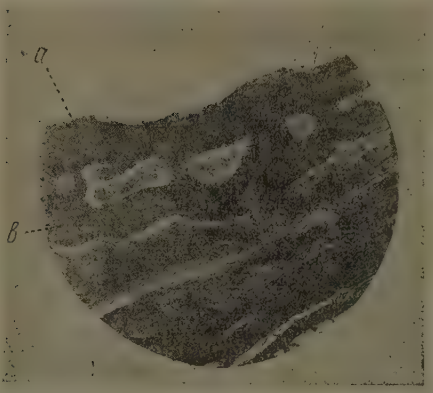


Fig. 1. Osseous wall of the cyst formed at the site of insertion of the mucous membrane of the bladder: *a*—epithelium, *b*—osseous tissue. Photo, × 80.

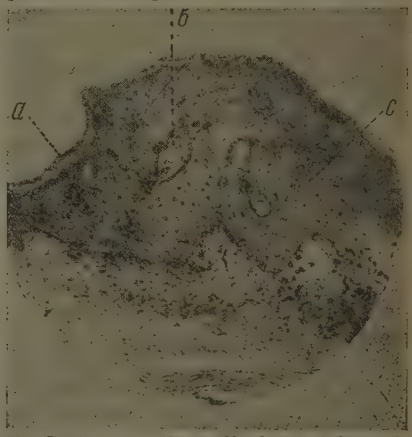


Fig. 2. Bone in the wall of a cyst formed at the site of insertion of the mucous membrane of the ureter: *a*—epithelium, *b*—connective tissue with osteoblasts, *c*—bone. Photo, × 80.

in other—two-storeyed. Immediately under it lay osseous tissue, separated from the epithelium only by thin layers of connective tissue (Fig. 1).

By analogy with the observations of N. V. Nassonov, it should be assumed that the mucous membrane of the bladder of a dog contains an organizing substance which is liberated in the course of the disintegration of the cells of this mucous membrane, under the conditions of its insertion into the subcutaneous tissue of the abdomen of the same dog. This organizing substance shows the only capacity to transform the surrounding connective tissue into bone; neither the destruction of the cutis, nor the proliferation of the cells of the epidermis was observed in our experiments.

To specify the conditions of the action of this organizing substance I attempted to transplant the mucous membrane of a dog, immediately after it was killed, to 4 other dogs (4 grafts to each dog). There was no bone-formation, the swellings at the sites of insertion were of an insignificant size and soon disappeared (these experiments were made at the Department of Patho-Physiology of the 3rd Moscow Medical Institute, in collaboration with Dr. Burachevsky). Besides this, I transplanted the mucous membrane of the bladder of a dog under the skin of the abdomen of the rabbit (one test), under the skin of the abdomen of the rat (one test) and under the skin of the brachium of human persons (4 tests). No bone-production was registered

in any of the cases. Non-specific granulation tissue appeared at the site of insertion which afterwards wealed. Thus, under heteroplastic conditions the activity of the organizing substance contained in the mucous membrane of the bladder remains undemonstrated.

With the view of testing other parts of the urinary ways for the presence of a bone-producing factor, I transplanted the mucous membrane of the ureter and of the kidney-pelvis under the skin of the abdomen of two dogs. Having extirpated under narcosis one of the kidneys together with the ureter, I separated from the tissue of the kidney five pieces of the mucous membrane of the kidney-pelvis, varying in size between $2 \times 3$ and $2 \times 4$ mm, and inserted these under the skin of the same dog, into pockets made on both sides of the operation wound. I have failed to separate the mucous membrane of the ureter from the other layers composing its wall, therefore the ureter was simply cut into bits of the same size and these bits were likewise inserted under the skin. In one of the dogs hard tumors, similar to those which we obtained by inserting the mucous membrane of the bladder, appeared at the site of insertion of the mucous membrane of the ureter. Having cut out these tumors 25 days later, I found them to be cystic structures with a preserved epithelial tegumen of intermediate type, paving the wall of the cyst from the inside; immediately under it lay osseous tissue of a periostal type of development. This osseous tissue contained cavities, filled with connective tissue elements, capillary vessels and typical osteblasts; osteoblasts accumulations can also be observed at the periphery of the new-formed bone (Fig. 2). Hence it can be assumed that the bone-producing substance is contained not only in the mucous membrane of the bladder of the dog, but in that of its ureter as well. The details of the histogenesis of the osseous tissue will be the subject of a special communication.

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*EVOLUTIONARY MORPHOLOGY*

# ON THE PHENOMENON OF REGRESSIVE CHANGES IN SOME BAR-WORM MOTHS (*PSYCHIDAE*)

By D. M. FEDOTOV

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A very favourable material for studying the problem of regressive evolution is found in Bag-worm Moths. The females of these insect are usually wingless and deprived of the fundamental features characteristic of the butterfly's external and internal structure, except vigorously developed reproductive system. The males have, however, normal wings and show but a few traces of regressive changes. Not only the process of ontogenesis, but even the structure of adult forms of Bag-worm Moths have been studied quite insufficiently, while their study provides many data of great interest.

Our knowledge concerning the organization and ecology of Bag-worm Moths is based chiefly on works dating as far back as the last century, especially on Hoffmann's work (1860), whose anatomical data I am now able to substantiate. In more recent investigations (e. g. Petersen, 1900) only some features of these forms' structure are dealt with, or else they are devoted chiefly to the biology and ecology of this group and to some extent to its taxonomic position. Yusbashyan (1930) is the only one who has presented some data concerning the development of Bag-worm Moths and, as far as I know, he continues working on this problem.

Two forms of Bag-worm Moths, namely *Pachytelia unicolor* Hufn. collected by G. M. Strogaya near Moscow, and closely related *Pachytelia* sp., which I collected at Sochi, were studied in the present work. The Sochi-form is much more convenient for work, since it gives two generations a year, while the development of the Moscow-form, *P. unicolor*, lasts two years. The fundamental features of the structure and development of these two forms being identical, I shall give in the present paper data concerning both of them without dwelling so far on the differences observed.

The similarity between the male and female larvae is so great that it is necessary to dissect them and to inspect their gonads in order to determine their sex. The male caterpillars have oval testes of a deep yellow colour, covered with a compact, dense layer of the fat body. The ovaries of the female caterpillars are flat, triangular in shape, not so brightly coloured, smaller than the testes, and have no flat body sheath. Four egg-tubes are distinctly seen through the transparent walls of the ovaries. So far as I could establish, the imaginal buds of the wing are present in larvae of all instars and have at the very beginning of larval development the form of small hypodermal thickenings with rudiments of tracheolae; adjacent to the imaginal

discs lay several undistinctly separated groups of blood-forming cells and parts of the fat body. The imaginal buds of the wing in male and female larvae develop differently, their development in males being quite normal, while in females it is retarded. The imaginal buds of the wing in males increase in size and through a process of invagination assume a form of sacs. Their thick upper wall gives rise to the wing rudiment, while the thin under wall forms the peripodial sac (Fig. 1, *A*, *B*). In large larvae the masses of the blood-forming cells become small, being spent in the process of development of the wing imaginal discs.

The development of wing's imaginal discs in female larvae is stopped with age, though, so far as I could establish, in young larvae the imaginal

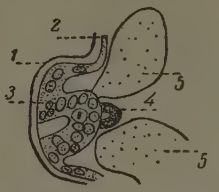


Fig. 2. Cross-section of wing imaginal bud of male larva of 2nd instar of *Operophthera brumata* L.: *1*—chitin, *2*—hypoderm, *3*—wing imaginal bud, *4*—tracheolae of bud, *5*—blood-forming cells; ×480.

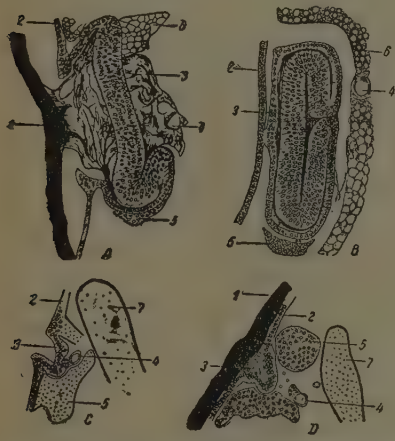


Fig. 1. Cross-sections of the imaginal buds of the wing of large larvae of *Pachytelia* sp.; same age and magnifications (×187). *A* and *B*—imaginal buds of a male at two different levels, *C* and *D*—imaginal buds of two female larvae. *1*—chitin, *2*—hypoderm, *3*—wing imaginal bud, *4*—tracheolae of the bud, *5*—blood-forming cells, *6*—fat body, *7*—muscles.

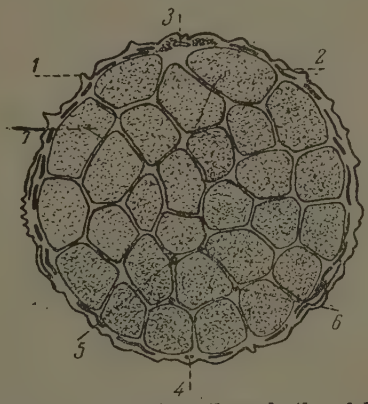


Fig. 3. Cross-section through the abdomen of a *Pachytelia unicolor* Hufn. female: *1*—body wall, *2*—body muscles, *3*—dorsal blood vessel with accumulations of nephrocytes on both sides, *4*—ventral nervous system, *5*—hind gut, *6*—Malpighian tubes, *7*—eggs; ×15.

buds are alike in both sexes. Owing to the stop of development of the wing's imaginal buds, in large female larvae they are found to be much smaller than in males. They have a form of small hypodermal invaginations (Fig. 1, *C*, *D*) with rudiments of tracheolae, and are surrounded with groups of blood-forming cells. In other words, the wing's imaginal buds in large female larvae of the Bag-worm Moths preserve the features characteristic of imaginal buds of the second instar larvae of forms having normal wings (Fig. 2). Such a state is chiefly due to the standstill of development of the wing's imaginal buds. However, in the last instar larvae there occurs also a degeneration of the distal parts of imaginal buds and of the tracheolae they are connected with. In addition to this the remaining parts of the wing's imaginal buds (small invaginations of hypoderm) apparently undergo before pupa-

tion a reverse process of levelling, all these three processes leading to the formation of pupae totally deprived of wings. Owing to the supression of wing development, the masses of blood-forming cells surrounding the wing's imaginal discs are not spent, which accounts for their preservation in large female larvae, while in male larvae of equal size they become scarcely visible. So far as I could find there is no difference in the development of other organs of male and female larvae, of course with the exception of the reproductive system.

At the time of pupation sharp difference can be noticed in the course of development of male and female larvae, which differed therefore only in respect to the imaginal discs of the wings. The male larvae are transformed in pupae which show normally developed wing cases and all cephalic and thoracic appendages, while the female larvae give rise to pupae with rudimentary cephalic and thoracic appendages, this reduction being apparently correlated with a complete reduction of wings. As it had been described by Hoffmann as early as 1860 and afterwards substantiated by a number of other investigators, such á pupa has small chitinous projections, cases which cover the vestiges of cephalic appendages and the strongly reduced thoracic legs. Through transparent chitin of the ventral part of the wall of the pupal body one can see the ganglia of the ventral nerve cord and on the 3rd, 4th, 5th and 6th segments—the vestiges of the larval abdominal legs. In contrast to all other larval organs the ovaries in the pupa develop very vigorously and assume in a short time their definitive form.

The complete loss of the wing rudiments and the extreme reduction of the cephalic appendages and thoracic legs in a female pupa lead to a modification of its body shape. A female pupa has a small head, three small thoracic segments and 10 abdominal ones. Adult females retain the same structure almost unchanged. They have a small head with almost completely reduced cephalic appendages, three thoracic segments with small, reduced, slightly differentiated functionless legs and a simply segmented abdomen. Only the 9th and 10th segments of the latter are morphologically differentiated being transformed in parts carrying the orifice of the bursa copulatrix as well as the genital and anal orifices. This differentiation is caused by the development of the definitive reproductive system.

Along with a simple segmentation of the body, hatched females retain a simple structure of the hypoderm consisting of a layer of low cells with thin chitin, the undifferentiated body muscles characteristic of caterpillars and playing an important rôle in the process of egg-laying (the push the eggs out of the long, twisted egg tubes), and, finally, a simple elongated form of the dorsal blood vessel. The morphology of the nervous system of a butterfly is also essentially similar to that of a larva. They consist both of a small brain and of a ventral nervous cord with a suboesophagial ganglion, three larger thoracic ganglia and eight abdominal ones. In most of the abovementioned organs, as for example in body muscles and in the peripheral parts of the nervous system, some regressive changes occur by the time of their transformation into definitive organs of an imago.

In a number of other larval organs undergoing transformation into a definitive form, regressive changes are very striking while the processes of metamorphosis are almost completely lacking. Antennae are reduced to minute, undifferentiated outgrowths on the head, mouth parts are transformed into small projections on its ventral part, the eyes, well developed in larvae, become reduced to irregular accumulations of pigment with a few crystallic cones. The strong legs of a larva become transformed, as it has been already pointed out, into small legs of a butterfly, showing a scarcely noticeable differentiation, but preserving the type of the structure of larval legs.

A number of profound changes occur at the pupal stage in the course of imago-formation. The intestine of a butterfly is of the same general type as that of a larva. In both of them it has a form of an almost straight tube, and oesophagus, crop, and a long mid-gut are present both in larva and in imago. But the mouth opening undergoes in the imago a complete atrophy, the most part of the intestine, especially the hind-gut, assume the form of an extremely narrow tube, the integrity of the epithelial walls of different parts of the intestine is disturbed, the epithelial walls of the intestine undergo a considerable reduction. All these phenomena are connected with the imago aphagy. The Malpighian tubes in the imago are well developed; unlike larval Malpighian tubes which open direct in the gut, they are connected with it by two common ducts, this being a general rule in butterflies. Thus, along with the standstill in the development and the reduction process, the intestine in the course of ontogenesis partly assumes imaginal features.

The only system which in the course of ontogenesis of these Bag-worm Moths shows progressive development, undergoing a complete metamorphosis, is the reproductive one. The small triangular ovaries of a larva are transformed in enormously developed ovaries of a butterfly. Each of the ovaries consists of four very long egg tubes. They occupy almost the whole body cavity and produce large eggs abundantly supplied with yolk (Fig. 3). As it was already found by Hoffmann (1860) and Petersen (1900), the ovaries, genital ducts and all parts of the reproductive system show a development typical for butterflies.

Thus, we can point out the following peculiarities in the ontogenesis of the female in the genus *Pachytelia*.

The development of female larvae proceeds in the same way as that of the male ones, except the imaginal buds of their wings which cease to develop in large female larvae, thus assuming the form of small invaginations of hypoderm. The stop of development, degeneration of the distal parts of the hypodermal invaginations—rudiments of wing imaginal buds, and, finally the process of levelling of these invaginations seem to precede pupation, lead to a complete atrophy of the wings. The complete atrophy of the wing buds in the pupa is connected with non-differentiation of its body into thorax and abdomen, the simple differentiation of the pupa persisting in the butterfly. Most of the larval organs do not undergo true metamorphosis and their development is retarded. Some of them, as the nervous and blood systems, muscles, integuments ans some parts of the intestine pass to the imago almost unchanged, undergoing but a slight regress, while others, like antennae, mouth parts, eyes, thoracic legs and other parts of the intestine become strongly reduced. Only the reproductive system, with its vigorously developed ovaries, undergoes a true metamorphosis. It would, however, be incorrect to believe, as several authors did, that female Bag-worm Moths are neotenic forms, since they show not only a stop of development in their ontogenesis, but regressive changes as well, the latter being particularly noticeable.

Data secured from the study of female Bag-worm Moths of the genus *Pachytelia* point to the fact that regressive changes play an important rôle in the process of evolution. Bag-worm Moths prove to be biologically progressive forms, in spite of the fact that the only progressively developing system in the females is the reproductive one. They are widely distributed throughout the world and successfully stand the struggle for life against their relatives which show a higher organization.

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*EVOLUTIONARY MORPHOLOGY*

# CORRELATION BETWEEN THE PROVISORY AND DEFINITIVE ORGANS OF *ASCIDIA* DURING THEIR METAMORPHOSIS

By L. ZHINKIN

*(Communicated by I. I. Schmalhausen, Member of the Academy, 28. VI. 1939)*

The freely swimming larva of the *Ascidium* is a very complex organism, composed of two different systems of organs: larval organs, built of highly differentiated cells, and definitive organs, constituted by undifferentiated embryonic cells containing yolk. After its egression from the egg envelopes the *Ascidium* larva, having swum for some time, attaches itself by its anterior extremity to some submersed object and goes through its metamorphosis. This metamorphosis consists in that the provisory organs of the larva (concentrated, with the exception of the nervous system, mainly in the tail) undergo reduction, while the definitive ones suffering displacements and differentiation give rise to the body of the solitary *Ascidium*. The coinciding in time of the disintegration of the provisory organs ond of the intense differentiation of the definitive ones, provides grounds for assuming the existense of a correlative dependence between these two systems of organs. One can suppose that the reduction of the provisory organs is necessary for the normal development of the definitive ones. The experiments described below were arranged to the purpose of elucidating the connexion between these two systems of organs. The experiment were conducted on the larvae and metamorphosis of the colonial *Ascidium Botryllus schlosseri* (Pallas).

The experiments were made at the Sebastopol Biological Station of the Academy of Sciences of the USSR. The eggs in *Botryllus* develop in the peribranchial cavity and but fully formed larvae which have reached a strictly definite stage of their development leave the colony. Consequently, every larva which has just left the colony, show identical structure. The main mass of the larvae becomes attached 1—3 hours after they have left the colony([1],[2]). Immediately after the larva is fixed, begin the drawing in of its tail and the changes in the mutual disposition of the organs. In the course of its reduction the tail shifts by 90° and the siphons assume apical position. This is due to the irregular growth of the mantle of the attached larva. The external changes are accompanied by the differentiation of the tissues. Under natural conditions the reduction of the tail is always preceded by the attaching of the larva and the alteration of it anterior end in connexion herewith. To disturb the connexion between the anterior end and the tail in a larva which has just left the colony, the anterior end was cut off. This operation involved the resection of the papillae, the anterior ends of the ampullae and the attaching membrane. Together with these were eliminated also five peripheral nervous ganglia, situated at the anterior end of the larva ([3]).

Thus, by this operation the nerve connexion between the anterior end and the trunk and tail was disturbed. It suffices sometimes for destroying the paths connecting the peripheral ganglia with the central nervous system to compress the anterior end of the larva with a needle or a lancet. The results of these tests were as follows. After the operation the larvae, as a rule, do not become attached, and this prevents most of them from going through their metamorphosis in a normal way. Moreover, a great number of the larvae operated upon retain their tails. In registering the results of the experiments, only those larvae which had fully retained their tails or had only just begun to draw them in were registered as having retained the tail. The results of the experiments 24 hours after the operation can be illustrated by the following figures. Out of 85 operated larvae 67 retained and 18 lost their tails (totally or partly).

The tail in the operated larvae does not function and, as this could be followed in preparations, the cells constituting it degenerate gradually. Similar tests were made by Holmgren (4) on larvae of *Clavelina*; it is to reg-

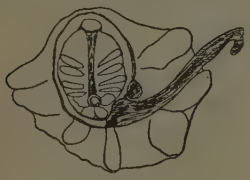

Fig. 1.

Fig. 2.

ret only that he did not register the disturbances caused by the operation in the body of the larva.

The presence of the tail in the operated larvae of *Botryllus* in my experiments, and in those of *Clavelina* in the experiments of Holmgren does not interfere with the normal development of the definitive organs. After a certain lapse of time the operated larva is transformed into a solitary *Ascidium* or a late larva, but retains its tail. The tail in these cases may be displaced laterally (Fig. 1), as this is observed normally, or else it continues to occupy the position it did in the larva (Fig. 2).

It is visible from this experiment that there exists a connexion between the anterior end of the larva and its tail, which seems to be realized via the nervous system; this connexion being disturbed, the tail fails to be reduced. At the same time the presence of the tail which is a provisory organ does not interfere in any way whatever with the development of the definitive organs. The larvae which have as the result of the operation preserved their tails, accomplish their transformation into normal solitary *Ascidia* and proceed to gemmulation. Of all the provisory organs such a larva retains only the tail, because the central nervous system suffers disintegration.

Observations on the metamorphosis of larvae placed under unfavourable conditions permitted to supplement the experimental data described above. Placing *Botryllus* larvae into Koch dishes, we often had the occasion to observe larvae which, having swum for 24 hours, neither attached themselves nor began their metamorphosis. Grave and Woodbridge (1) examined a larva of *Botryllus* which had swum for 24 hours and found it to not differ in its structure from those which had swum for only 1—2 hours. I collected a number of such larvae which had swum for 24 hours or more without passing to their metamorphosis. Studying the structure of such larvae, it is easy to note that among them there are individuals which actually have not begun their metamorphosis, but there are also many others, in which defi-

nitive organs develop like in case of normal metamorphosis. The differentiation begins with the development of the hypophysis, this is followed by the development of the definitive nervous ganglion, endostyle and other organs. The development of the definitive organs goes on in spite of the presence of the provisory nervous system in the tail, thanks to which the larva is swimming all the time. In one case we observed a larva swimming freely with the aid of its tail, while already both siphons had formed in it and its digestive system functioned normally. Particularly numerous are larvae which have already begun their metamorphosis without losing their tail, if the larvae are placed into contaminated or badly aerated water. The lack of oxygen seems to exert an unfavourable influence on the larvae; there can be no normal metamorphosis without oxygen. Studying in preparations the structure of the tail of larvae which had been swimming for 24 hours or more, it is possible to see that the cells it is composed of look like normal cells, and no degenerative phenomena can be detected in them.

Considering the facts described above, the conclusion seems justified that in the larva of *Botryllus* the morphogenetic connexion (5) between the provisory and definitive organs is absent. Individual stages of metamorphosis can be eliminated without noticeably affecting the final results of the larva's metamorphosis. The attaching of the larva, the reduction of the provisory organs are no obligatory conditions either in the normal development of the definitive organs or in the formation of the solitary *Ascidium*. These conclusions are corroborated by the results of Child (6) who observed cases of absence of the larval stage in *Corella*. Weiss (7) observed the development of definitive organs without the reduction of the provisory ones in *Cyona* subjected to the effect of narcotics. All these facts considered together make us believe that the absence of a correlative dependence between the provisory and the definitive organs is common to all the freely swimming larvae of *Ascidia*.

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*EVOLUTIONARY MORPHOLOGY*

# ALTERATION OF THE REGENERATIVE POWER OF THE LARVAE OF *ASCIDIA* DURING METAMORPHOSIS

By L. ZHINKIN

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*Ascidia* offer an example of those organisms which, showing mosaic development (1), regenerate readily in adult state. The capacity for regeneration suffers abrupt changes in different animals in the course of their ontogenesis and proves to be closely connected with the processes of differentiation taking place in the organism. Is seemed interesting, therefore, to study the variations of the regenerative power of *Ascidia* in the course of their post-embryonic development.

Conklin has shown that a defective larva develops from a half of the egg of a *Cyntia*, this defect not being restored at later stages of development. Later on, it is true, Schmidt (2) found certain regulative phenomena in the ectoderm of the hemiembryos of *Cyona*.

I have studied the regulative capacity of the late development stages, beginning with the freely swimming larva and ending with the solitary *Ascidium*. The experiments were conducted at the Sebastopol Biological Station of the Academy of Sciences of the USSR. Larvae of the colonial *Ascidium Botryllus schlosseri* (Pallas) were used as test objects. The larvae of *Botryllus* develop in the peribranchial cavity and leave the maternal organism always at a strictly definite stage of their development. I subdivided the whole postembryonic period of development into four stages (Figs. 1, 2 and 3), each of which was investigated in detail.

The first stage (Fig. 1) was the freely swimming larva, having just left the colony. Both provisory and definitive organs of such larvae were injured for provoking a defect. The larvae of *Botryllus* were dissected along different planes, the dissection involving almost every organ. When the tail (a provisory organ) was cut off, the chord, striped muscles, nervous system, mantle and tunica were injured. No regulative phenomena were observed after such injury either on the part of the tail as a whole, or on that of the individial tissues composing it. Only the tunica unites at the border of the cut closing up the wound. After the injury the motions of the tail cease; this, however, does not prevent its normal reduction. If the anterior end is cut off, no regeneration ensues either. All the provisory organs, consisting of highly differentiated tissues, are incapable of regeneration. The definitive organs of the freely swimming larva consist of embryonic cells filled with yolk, which fail to compensate for the defect after injury. The defect, caused by the cutting off of several ampullae, remains as such until the end of the

metamorphosis. A cut-off siphon is not restored and a larva with one siphon making through its metamorphosis is the result. Injuries of endostyle, intestine, stomach, branchial fissures are never restored. However, the defect of one organ does not hinder the normal development of the rest of the organs of the freely swimming larva. Ciliate cells are formed in the endostyle in every case. All the organs of the injured larva differentiate, without, however, attaining advanced stages, which is observed in adult *Ascidia*. We happened to observe differentiation of the (definitive) nervous ganglion in larvae, in which all the rest of organs had been almost entirely destroyed.

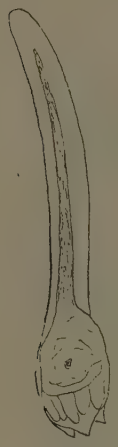

Fig. 1.

Fig. 2.

Fig. 3.

Gemmulation takes place in almost every case, whatever the injury inflicted on the freely swimming larva, the formation of the bud proceeding at the expense of the atrial vesicles. As a rule, the development of the bud does not reach its final stage. This may be explained by the fact that the larva does not feed and the yolk is soon spent. It is evident from the data briefly described above that the definitive organs of the freely swimming larva are highly autonomous in their development. Great autonomy is shown also by the process of gemmulation.

We classified as belonging to the second stage (Fig. 2) those larvae which had lost their tail and had become attached to the substratum. But the siphons of the larva at the 2nd stage have not yet burst and such a larva cannot feed. Simultaneously with the loss of the tail, the siphons are displaced, shifting from a lateral to an apical position. The cells of such a larva have already passed through a certain differentiation and have lost a considerable part of their yolk. At the 2nd stage the larva possesses a certain regulative ability. 24 hours after the operation a certain number of larvae with a normal structure can be found. Such larvae show a response of the whole organism to the injury. A marked alteration of the outward aspect of the cells appears (the cells increase in size, stain differently). It is possible to observe the formation of individual organs, e. g. of the nervous ganglion. However, as well as at the preceding stage, ampullae are never restored. Total regulation is observed but rarely in larvae of the 2nd stage, and usually only small defects are restored. The lack of feeding at this stage is possibly one of the factors hindering regeneration in the injured larvae. The second factor hindering regeneration is gemmulation. A certain dependence is observed to exist between the growth of the bud and regeneration, the intensive growth of the bud seeming to hinder the process of regeneration. In some cases we were able to observe even the degeneration of the maternal organism at the time of an intensive growth of the bud. The above data induce on the think that the larvae of the 2nd stage possess already a capacity towards regeneration and under favourable conditions may supplement the defect inflicted upon them.

To the third stage (Fig. 3) we refer the larvae which outwardly resemble the solitary *Ascidia*, preserving at the same time a number of larval characteristics. The siphons of such larvae are still drawn together, but normally function together with the entire digestive system. Their branchial fissures just begin to form prostigmae and to transform into the defini-

tive branchial fissures. There is always a small bud near such a larva. The results of several series of tests show, as this should be anticipated, that such larvae regenerate rather speedily and completely.

To illustrate the above said I shall cite one of the tests conducted on larvae of the 3rd stage. Larvae attached to the bottom of a Koch dish were dissected between the oral and anal siphons for this test. A total number of 24 larvae was operated upon. 24 hours after the operation 14 larvae regenerated, 9 did not degenerate, 1 died. Part of those which failed to regenerate have merely had no time to restore completely the piece they had lost. Others failed to regenerate owing to the intense development of the bud. In two cases we were able to observe the development of the bud to depress that of the maternal organism to such a degree that there was no regeneration whatever; two days later the bud developed into a solitary *Ascidium*. The results of the experiment just described coincide with those of a number of other tests involving larvae of the third stage. I think it therefore unnecessary to dwell upon them.

We classed among the 4th stage the solitary individuals of *Botryllus*. Only a small number of experiments were arranged with these organisms and we do not think it necessary to dwell upon them, since the larvae of the 3rd stage already show a conspicuous capacity for regeneration.

Comparing the tests made on larvae of various stages, we must note first of all that the larvae of the 1st stage are totally incapable of regeneration. With the progress of the metamorphosis and of tissue differentiation the larvae of the subsequent stages begin to regenerate, at first apparently rather feebly, later on with sufficient speed and completeness.

The absence of the regeneration of provisory organs is easy to understand, since they are composed of highly differentiated cells which have already lost the ability to proliferate. The absence of regulation in the definitive organs, on the other hand, may be explained only by their mosaic structure and by the absence of the response of the whole to injury. With the outset of the metamorphosis of the *Botryllus* larva this mosaic character of its structure disappears and the regulative capacity comes to the forefront. The process of gemmulation in the freely swimming larva is going on independent of the development of its individual organs, being to a considerable degree autonomous. At late stages of the metamorphosis, however, gemmulation does not seem to possess this autonomy, and the intense development of a bud depresses regeneration in larvae of the 3rd stage.

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*MYCOLOGIE*

# LA RÉSISTANCE COMPARÉE DE L'AUBIER ET DU BOIS PARFAIT DE L'ÉPICÉA ET DU SAPIN À L'ACTION DU CHAMPIGNON DES CHARPENTES (*PORIA VAILLANTII* Fr.)

Par ANDRÉ A. YATSENKO-KHMÉLEVSKY et NICOLAS N. BRÉGADZÉ

*(Présenté par A. A. Richter, de l'Académie, le 12. VI. 1939)*

La partie intérieure du tronc des arbres—le duramen ou le coeur—est caractérisée par la durabilité supérieure à celle que possèdent les parties périphériques du tronc—l'aubier. Cette différence est due à l'accumulation dans le duramen des substances antiseptiques, se rapportant, pour la plupart, au groupe des tannides et qui déterminent la coloration intense du bois de coeur.

Cette propriété du bois de duramen est trés estimée dans la pratique et c'est à elle que le bois des essences possédant le duramen (pin, mélèze, chêne, etc.) doit ses qualités supérieures comme bois de construction.

Il était intéressant d'établir la présence de la même différence dans le bois des essences qui, privées du duramen, possèdent le bois parfait, c'est-à-dire des essences chez lesquelles la partie centrale du tronc, ne différant de la partie périphérique par la coloration du bois, en diffère par une sécheresse marquée. La Section d'Anatomie et de Physiologie Végétale de l'Institut Botanique de Tbilissi a entrepris une série d'études sur les propriétés du bois parfait. Ce travail est une des parties de cette étude.

La littérature forestière, très pauvre en général d'observations sur les propriétés du bois parfait*, ne nous offre pas de données sur sa résistance comparée à l'action du champignon. On trouve des indications[1] que dans les troncs du hêtre sur pied, c'est la partie centrale (le bois parfait) qui est affectée particulièrement par les champignons (la formation du faux-coeur du hêtre). Néanmoins, ces observations, d'ailleurs vraies aussi pour d'autres essences possédant le bois parfait, ne prouvent pas que l'aubier soit plus durable que le bois parfait, car dans les troncs des arbres sur pied la propagation des gyphes des champignons dans la périphérie du tronc (dans l'aubier) est généralement rendue difficile (voire impossible) par la haute humidité du bois de cette partie du tronc. Donc, la solution du problème de la durabilité comparée de l'aubier et du bois parfait ne peut être obtenue que par expériences de laboratoire.

Pour nos expériences nous avons choisi le bois de sapin du Caucase (*Abies nordmanniana* Spach.) et de l'épicéa orientale (*Picea orientalis* Carr.), les essences qui possèdent le bois parfait bien caractérisé. Comme champignon destructeur nous avons choisi le champignon des charpentes *Poria*

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* Il est intéressant de noter que le terme même «bois parfait» n'a pas sens exact dans la littérature forestière française et anglaise.

*Vaillantii* Fr. qui est le destructeur le plus énergique des constructions en bois dans la R. S. S. de Géorgie.

Les échantillons pour notre étude ont été préparés du bois conservé dans notre laboratoire durant 5 ans et qui possédait à peu près 10% d'humidité. Pour chaque essence nous avons pris le bois de deux arbres, tous les quatre arbres ont été coupés dans les environs de Borjomi (R. S. S. de Géorgie), dans les conditions du milieu ambiant analogues, à peu près d'un même âge (50—60 ans) et d'un même diamètre (30—40 cm). Poup chaque arbre, les échantillons furent choisis dans 4 endroits différents—au centre du bois parfait, dans les limites extérieures du bois parfait (en voisinage avec l'aubier), dans les limites intérieures de l'aubier (en voisinage avec le bois parfait) et à la périphérie de l'aubier, près de l'écorce, 25 échantillons pour chaque endroit choisi. La quantité totale des échantillons atteignait 400. La dimension de chaque échantillon était à peu près de $1.5 \times 1.5 \times 3.5$ cm. Avant de placer les échantillons sur le mycélium, ils étaient pesés avec une précision d'une dixmillième de gramme. Pour la détermination de l'humidité nous avons pris, en outre, 32 échantillons, 2 échantillons de chaque endroit choisi, et les moyennes obtenues étaient considérées comme caractérisant l'humidité de tous les échantillons de l'endroit. Les données sur l'humidité sont réunies dans la table 1 (en %).

Table 1

| | | Centre du bois parfait | Limites extérieures du bois parfait | Limites intérieures de l'aubier | Périphérie de l'aubier |
|---|---|---|---|---|---|
| Sapin | I | 9.04 | 10.65 | 10.55 | 10.20 |
| | II | 9.56 | 9.54 | 10.21 | 10.77 |
| Epicéa | I | 10.91 | 11.75 | 11.69 | 11.21 |
| | II | 11.43 | 11.22 | 11.38 | 11.43 |

Comme substratum pour les champignons, nous avons pris le moût de bière avec l'agar-agar dans des bocaux ordinaires de 200 $cm^3$. Lorsque le mycélium avait couvert tout le substratum, les échantillons étaient placés dans les bocaux, mais préalablement on les essuyait avec de l'ouate mouillée d'alcool et on les grillait. L'inoculation a été faite le 3 et le 5 juin 1938 et les échantillons ont été laissés dans les bocaux jusqu'au milieu du mois de novembre, c'est-à-dire durant 4 mois et demie. Après la fin de l'expérience, les échantillons ont été tirés des bocaux, nettoyés du mycélium, séchés danc un thermostat à 100°C, jusqu'à ce qu'ils aient atteint le poids absolument sec, et pesés. Vu que les données de la première pesée (avant l'inoculation) se rapportaient à des échantillons possédant un certain degré d'humidité (table 1), ils ont été recomptés pour recevoir leurs poids absolument sec. La perte du poids qui caractérise le degré de la destruction du bois était calculée en pour-cent.

Dans chaque bocal on plaçait 8 (parfois 10) échantillons, par 2 échantillons de chacun des quatre endroits choisis, chaque bocal formant une série. Nous avons préparé 44 séries, mais dans quelques bocaux le champignon n'a pas couvert les échantillons et ces séries (contenant 40 échantillons) n'ont pas été analysées. Dans la plupart des bocaux, le développement du champignon n'a pas été uniforme non plus; dans quelques séries tous les échantillons étaient couverts entièrement, dans d'autres ils ne l'étaient que partiellement. Puisque dans chaque bocal le champignon couvrait tous les échantillons à peu près au même degré et vu que notre étude avait pour but d'établir la résistance comparée du bois pris dans les endroits dif-

férents du tronc, la différence du développement du champignon dans des bocaux différents n'a pas pu influer sur les résultats reçus. Les échantillons entièrement couverts ont montrés aussi les pertes du poids différentes.

Les fluctuations importantes des données obtenues nous ont obligé à recourir aux méthodes de la statistique variationnelle. Les résultats obtenus sont réunis dans la table 2. En analysant les chiffres de la table 2 nous voyons que le bois du sapin ne montre aucune régularité dans ses propriétés de résistance contre l'action du champignon et ainsi le bois parfait et l'aubier du sapin ne diffèrent guère sous ce rapport.

Table 2

| | | Bois parfait | | | | Aubier | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Centre | | Limites extérieures | | Limites extérieures | | Périphérie | |
| | | $M_1 \pm m_1$ | $\sigma$ | $M_2 \pm m_2$ | $\sigma$ | $M_3 \pm m_3$ | $\sigma$ | $M_4 \pm m_4$ | $\sigma$ |
| Sapin | I | 17.7±2.5 | 9.83 | 14.8± 2.1 | 8.48 | 16.3±1.7 | 6.93 | 11.9±1.7 | 6.44 |
| | II | 6.7±1.7 | 5.95 | 12.8±10.3 | 40.1 | 9.9±2.0 | 7.86 | 10.6±1.5 | 6.04 |
| Epicéa | I | 5.8±1.1 | 3.99 | 6.3± 1.3 | 4.46 | 10.1±1.7 | 5.91 | 10.4±1.8 | 6.41 |
| | II | 5.9±0.9 | 3.95 | 3.8± 0.7 | 3.0 | 6.9±1.2 | 5.14 | 8.0±1.4 | 6.09 |

Dans l'épicéa, au contraire, dans tous les cas on remarque que le bois parfait montre en comparaison avec l'aubier une perte de poids moindre, ce qui indique que le bois parfait est plus résistant à l'attaque des champignons. Néanmoins, l'analyse du caractère essentiel de ces différences selon la formule

$$t = M_2 - M_3 : \sqrt{m_2^2 - m_3^2}$$

nous donne, dans le cas de l'épicéa I (où nous avons les différences les plus marquées) $t$ égal au 1.8, tandis que pour avoir une certitude entière sur la validité de ces différences, $t$ doit être égal au moins au 3.

La différence dans la résistance de l'aubier et du bois parfait doit être plutôt attribuée à des modifications que subissent les parois cellulaires du bois parfait dans le processus de sa formation. Il faut ajouter que les différences établies entre la résistance du bois parfait et l'aubier de l'épicéa ne sont pas grandes et doivent être sans importance pour la pratique.

Le bois de sapin est connu dans la pratique comme cédant très vite à la carie. Notre étude aussi montre une différence notable entre la durabilité du bois de sapin et du bois de l'épicéa. Les chiffres données par la table 2 ne donnent pas le tableau exact, car les moyennes ont été établies sur tous les échantillons, y compris les échantillons qui n'étaient couverts qu'à moitié par le champignon. Si l'on considère seulement les échantillons complètement couverts par le champignon, on trouve la perte moyenne du poids pour le bois de sapin égale à 19.3% (48 échantillons) et pour le bois de l'épicéa—9.7% (32 échantillons), ce qui veut dire que le bois de sapin est de deux fois moins résistant à l'attaque du champignon des charpentes que le bois de l'épicéa.

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Filiale géorgienne de l'Académie des Sciences de l'URSS.

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*PALÉONTOLOGIE*

# NOUVEAUX GENRES DE CORAUX *TABULATA* DU PERMIEN INFÉRIEUR DE L'OURAL ET DU BASSIN DU DONETZ

Par N. YAKOVLEV, membre correspondant de l'Académie

## FAMILLE DES FAVOSITIDAE

*Monotubella* gen. nov. Petits polypiers tubulaires cylindriques ou cylindroconiques, se fixant par leur extrémité inférieure, à planchers plats assez distants l'un de l'autre, avec murailles présentant à l'intérieur des traces de cloisons rudimentaires. Corail solitaire, mais quelques rares échantillons donnent naissance par gemmation latérale à un individu n'atteignant pas les dimensions de l'individu-mère; les cavités viscérales des deux individus communiquent entre elles (fig. 1) par une ouverture située à la base du plus petit. La surface extérieure est couverte de lignes d'accroissement.

Il nous semble que la forme décrite peut être rapprochée du genre *Romingeria* Nicholson (1879), qui en diffère par le fait que l'individu-mère produit d'assez nombreux individus, disposés en verticilles comme les rameaux des *Equisetum*. On observe en outre chez *Romingeria* qu'au cas où les branches se touchent ne serait-ce que localement, leurs cavités entrent en communication par des pores traversant les murailles, ce qui permet de ranger *Romingeria* dans les *Favositidae* et non dans les *Syringoporidae*. Notre forme n'a qu'une seule branche rudimentaire et il ne peut donc pas exister de pores sur les côtés. On peut admettre que le genre *Monotubella* est issu d'une forme coloniale plus compliquée par voie de dégénérescence consistant en un passage régressif de l'état colonial à l'état solitaire.

L'unique forme connue à ce jour avec laquelle la nôtre puisse être comparée est *Vermetus tschernyschewi* Stuck. du Permocarbonifère de l'Oural, rapporté à tort au genre *Vermetus*, qui possède, il est vrai, un semblant de planchers, mais concaves et situés seulement dans la partie supérieure enroulée en spirale de la coquille. La forme ouralienne se distingue toutefois de la nôtre par un diamètre beaucoup plus grand du polypier (diamètre de notre forme environ 3 mm, diamètre de la forme ouralienne max. 10 mm).

*Monotubella permiensis*, comme j'ai nommé la forme en question, a été trouvée dans le complexe dolomitique du Permien inférieur sur la rivière Makatikha dans le bassin du Donetz.

*Monotubella tschernyschewi* Stuck. a été recueillie par moi dans l'Artinskien de Krasnooufimsk, à l'état de deux fragments de la partie inférieure du polypier, adhérant par leur extrémité inférieure à des fragments de crinoïdes. Sur l'un d'eux une coupe dans le sens longitudinal a décelé la présence d'un plancher approximativement au milieu de la longueur du fragment. Stuckenberg, l'auteur de l'espèce ouralienne, n'a pas trouvé la partie initiale du polypier avec le point de fixation.

*Monotubella* n'est donc connue pour le moment que du Permien inférieur de l'URSS.

*Pseudofavosites* Gerth 1921. Ce genre, établi du Permien de Timor par

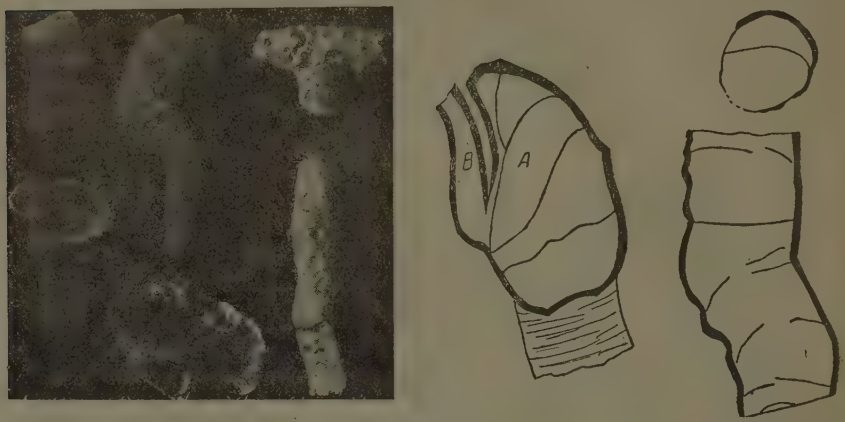


Fig. 1. Sur le fond clair coupes (grossies) et photographies (×2.5) de *Monotubella permiensis* n. gen. n. sp. Sur le fond sombre aspect extérieur et coupe transversale de trois fragments d'*Oculinella Gerthi* n. g. n. sp. Sur les coupes de *Monotubella* à droite échantillon avec individu *B* séparé par bourgeonnement; sur les photographies de *Monotubella* à gauche en haut échantillon avec cicatrice de fixation à la partie inférieure; la coupe d'*Oculinella* (photographie, × 10) montre dans la section transversale du polypier trois calices.

Gerth, se distingue de *Favosites* par l'absence de planchers et accessoirement par la présence d'excroissances épineuses près de l'aperture des cellules, dans les angles formés entre elles. L'espèce décrite ci-après provient de Krasnoouﬁmsk dans l'Oural, de l'horizon à crinoïdes. Ce genre était inconnu jusqu'ici dans l'URSS.

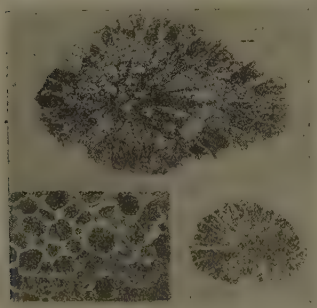

Fig. 2. *Pseudofavosites minus* n. sp. Coupes radiales de deux polypiers (×2), le plus petit avec pores dans les murailles, le plus grand avec planchers, et partie de la surface extérieure d'un troisième échantillon (grossi), avec orifices des calices. Les pores et les planchers se distinguent mieux à la loupe.

*Pseudofavosites minus* n. sp. Polypiers de forme variée, irrégulière, sphéroïdale, parfois à base aplatie recouverte alors d'une épithèque à rides concentriques. Comme à Timor, il existe des individus en symbiose avec des crinoïdes, chez nous toujours avec *Platycrinus*, semble-t-il; dans ce cas, les colonies du corail se fixent d'abord sur un côté de la tige du crinoïde, puis, en s'accroissant embrassent la tige sur tout son pourtour. La colonie a alors une forme sphérique ou irrégulière, étirée transversalement à la tige et assez souvent plus ou moins triangulaire en plan. On peut supposer qu'un angle (ou saillant) se développait à la rencontre du courant d'eau, tandis que le côté opposé déporvu de saillant s'accroissait le moins. Ainsi était réalisées les meilleures conditions pour l'aération de la colonie et peut-être aussi pour son alimentation. Un effet analogue était obtenu par la symbiose avec *Platycrinus*, qui avait la préférence probablement à cause de la mobilité particulière de sa tige.

Un trait intéressant non-observé chez l'espèce de Timor est la présence par endroits de planchers à l'état de dégénérescence, de résorption, ce qui se traduit par la minceur extrême des planchers ayant perdu la forme plane qu'ils ont chez *Favosites*, ancêtre incontestable de *Pseudofavosites*. La forme des planchers à juger d'après leur coupe en section radiale (fig. 2) est fort irrégulière, ridée, et la ligne de coupure rappelle les courbes caractérisant les mouvements oscillatoires, par exemple les courbes sismiques. Outre les planchers, peu nombreux il est vrai, qui s'étendent sur tout le diamètre de la section, il en est qui ne sont développés ou conservés que partiellement.

On peut considérer la forme décrite soit comme un *Favosites* en voie de transformation en *Pseudofavosites*, soit comme *Pseudofavosites* gardant encore des traces de sa descendance de *Favosites*. Notre *Pseudofavosites* a donc un caractère plus primordial que l'espèce de Timor. L'auteur a déjà eu l'occasion de signaler le caractère plus primitif de certains genres de crinoïdes de cette faune en comparaison avec celle de Timor (genres *Hemiindocrinus*, *Hemimollocrinus* Yakovl., etc.). Il a émis alors la supposition que l'âge de la faune de Krasnooufimsk devait être, par conséquent, au moins un peu plus ancien que celui de la faune de Timor. Le diamètre maximum de la colonie de *P. minus* est de 15 mm environ. Les cellules des polypiers atteignent à l'embouchure 2 mm de diamètre tout au plus, comme dans l'espèce de Timor.

### FAMILLE DES TRACHYPSAMMIDAE

Herth a décrit du Permien de Timor le nouveau genre *Trachypsammia* (1921), pour lequel il a établi la nouvelle famille des *Trachypsammidae*, qui se distinguent de tous les *Anthozoa* paléozoïques par leur aspect général et la structure de leur squelette, de sorte qu'on peut les comparer aux *Hexacoralla*, notamment aux *Oculinidae* et aux *Eupsammidae*, dont ils diffèrent, il est vrai, par l'absence de cloisons. Nous créons encore un nouveau genre—*Oculinella*, et en dépit du manque des cloisons, qui ont pu ne pas exister chez les formes ancêtrales, nous croyons à un lien avec les *Hexacoralla*.

*Oculinella* gen. nov. *Oculinella* diffère de *Trachypsammia* en ce que chez la première les cellules des polypes sont disposées plus ou moins régulièrement sur toute la surface du polypier cylindrique colonial, alors que chez la seconde elles sont placées en deux rangées situées sur les côtés opposés du polypier; la différence entre *Trachypsammia* et *Oculinella* en ce qui concerne la disposition des cellules est la même qu'entre *Enallohellia* et *Oculina*.

*Oculinella Gerthi* n. gen. n. sp. Polypier cylindrique, à section transversale elliptique, faiblement ramifié du côté du long axe de l'ellipse; la surface du polypier est parsemée de cellules de polypes, dont le diamètre est égal au tiers environ de celui du polypier. La surface du polypier dans les intervalles entre les cellules est granulée ou striée avec creux punctiformes entre les granulations et les stries. La structure microscopique du squelette est grenue, comme on peut en juger d'après la lame mince transversale de la fig. 1 qui recoupe trois cellules adjacentes. Une lame mince longitudinale du polypier, bien qu'en mauvais état de conservation, permet de voir que les corallites divergent à partir de l'axe longitudinal du polypier, s'incurvant vers sa surface et vers l'une de ses extrémités, évidemment vers l'extrémité libre. Bords des calices aigus, saillant à la surface du polypier. Diamètre des cellules 1 mm environ, diamètre du polypier dans le sens de sa plus grande largeur 2.5 mm environ. On ne possède que des fragments de polypiers sans extrémités distale et proximale. Provient de Krasnooufimsk, de l'horizon à crinoïdes de l'Artinskien.

Après l'envoi à l'imprimerie de mon mémoire «Nouveaux genres de coraux *Tabulata* du Permien inférieur de l'Oural et du bassin du Donetz», B. Likharev, qui en avait connaissance, me fit savoir que le corail *Monotubella*, au sujet duquel j'avais fait une communication il y a beaucoup d'années à la Société Paléontologique de Russie, a été décrit par G. Porfirjev dans le Bulletin «Pour le pétrole bachkire» (1937, № 6), où le *Vermetus tschernyschewi* Stuck. ouralien est rapporté par Porfirjev, comme chez moi, aux *Tabulata*. Porfirjev donne à *V. tschernyschewi* le nouveau nom générique de *Seleucites*, qui doit donc, en vertu des règles de priorité, remplacer le nom de *Monotubella* que je lui ai attribué. Porfirjev n'avait pas à sa disposition les parties initiales du polypier et n'a pas observé de gemmation, qui existe dans mes échantillons de *Seleucites permiensis* n. sp. du Bassin de Donetz.

Institut Central de Géologie.

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